Inorg. Chem. **2003**, *42*, 821–826

Inorganic Chemistry
Article

New Heterometallic Coordination Polymers Self-Assembled from Copper(II) Nitrate and (Diamine)Pt^{II}(pyridinecarboxylates)$_2$

Rita Song,[†] Kwan Mook Kim,*[,†] and Youn Soo Sohn*[,‡]

Inorganic Chemistry Laboratory, Korea Institute of Science and Technology,
Seoul 130-650, Korea, and Department of Chemistry, Ewha Womans University,
Seoul 120-750, Korea

Received July 24, 2002

One-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D) coordination polymers were prepared by self-assembly of binary metal complex systems, copper(II) nitrate and (en)Pt^{II}(nic)$_2$ or (dmpda)Pt^{II}(isonic)$_2$ (en = ethylenediamine, dmpda = 2,2′-dimethyl-1,3-propanediamine, nic = nicotinate, and isonic = isonicotinate), in aqueous solutions. Equimolar reactions of copper(II) nitrate with (dmpda)Pt^{II}(isonic)$_2$ and (en)Pt^{II}(nic)$_2$ resulted in 1-D $\{[(dmpda)Pt(isonic)_2Cu(OH_2)_3](NO_3)_2\}_n$ (**1**) and 2-D $\{[(en)Pt(nic)_2Cu(OH_2)](NO_3)_2\}_n$ (**2**), respectively, but the reaction of (en)Pt^{II}(nic)$_2$ with excess copper(II) nitrate gave 3-D $\{[((en)Pt(nic)_2)_3Cu_5(OH)_2(OH_2)_6](NO_3)_8\}_n$ (**3**). The local structure of crystal **1** has a mononuclear copper unit, **2** has a dinuclear copper unit with a Cu–Cu distance of 2.659(5) Å, and **3** has a pentanuclear copper unit. The methyl groups of the dmpda ligand are located in the space between two isonicotinate ligands of **1**, which is presumed to be an important factor to determine the final structure of the crystal formed by self-assembly. Magnetic behaviors of crystals **1**–**3** examined in the temperature range of 4–300 K appear to be governed by the local structures around the copper(II) ions and do not indicate any significant long-range magnetic exchange interactions along the polymeric chain.

Introduction

The crystal engineering of coordination polymers is currently of interest[1] because of the theoretical aspects related to the topologies of novel networks and their potential physicochemical properties such as electrical conductivity,[2] magnetism,[3] and applications to host−guest chemistry[4] and catalysis.[5] The self-assembly of organic ligands with inorganic metal ions is an efficient and widely utilized approach for the construction of organic/inorganic coordination polymers. Although the frameworks with versatile shapes such as simple chains,[6] ladders,[7] and sheets[8] have been reported so far, heterometallic coordination networks are of minority. The heterometallic networks were usually obtained by using

---

* Author to whom correspondence should be addressed. E-mail: yssohn@ewha.ac.kr.

[†] Korea Institute of Science and Technology.

[‡] Ewha Womans University.

(1) For recent reviews see: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107. (c) Blake, A. J.; Champness, N. R.; Hubberstey, H.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (d) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *31*, 319. (e) Fujita, M. *Chem. Soc. Rev.* **1998**, *27*, 417. (f) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461. (g) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(2) (a) Aumuller, A.; Erk, P.; Klebe, G.; Hünig, S.; von Schütz, J. U.; Werner, H. P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 740. (b) Ermer, O. *Adv. Mater.* **1991**, *3*, 608 and references therein.

(3) (a) Mathevet, F.; Luneau, D. *J. Am. Chem. Soc.* **2001**, *123*, 7465. (b) Miller, J. S. *Inorg. Chem.* **2000**, *39*, 4392. (c) Munno, G. D.; Munoz, M. C.; Julve, M. *Inorg. Chem.* **1992**, *30*, 2701.

(4) (a) Soldatov, D. V.; Ripmeester, J. A. *Chem. Mater.* **2000**, *12*, 1827. (b) Yuge, H.; Noda, Y.; Iwamoto, T. *Inorg. Chem.* **1996**, *35*, 1842. (c) Kitazawa, T.; Nishikiori, S.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 1029.

(5) (a) Abrantes, M.; Valente, A.; Pillinger, M.; Goncalves, I. S.; Rocha, J.; Romao, C. C. *J. Catal.* **2002**, *209*, 237. (b) Tannenbaum, R. *J. Mol. Catal. A: Chem.* **1996**, *107*, 207. (c) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

(6) (a) Batsanov, A. S.; Begley, M. J.; Hubberstey, P.; Stroud, J. *J. Chem. Soc., Dalton Trans.* **1996**, 1947. (b) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.

(7) (a) Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *Chem. Commun.* **1997**, 2027. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972. (c) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Inorg. Chem.* **1999**, *38*, 2259. (d) Fujita, M.; Kwon, Y.-J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. (e) Carlucci, L.; Ciani, G.; Proserpio D. M. *New J. Chem.* **1998**, 1319. (f) Fujita, M.; Sasaki, O.; Watanbe, K.; Ogura, K.; Yamaguchi, K. *New J. Chem.* **1998**, 189.

10.1021/ic0204777 CCC: $25.00

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

	1	2	3
empirical formula	$C_{17}H_{32}CuN_6O_{15}Pt$	$C_{14}H_{22}CuN_6O_{13}Pt$	$C_{21}H_{39}Cu_{2.5}N_{10}O_{26}Pt_{1.5}$
fw	819.12	741.01	1299.11
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)	$C2/c$ (No.15)
a, Å	10.105(3)	12.4972(18)	24.042(8)
b, Å	18.133(3)	13.700(3)	12.490(4)
c, Å	15.590(5)	15.442(2)	31.150(7)
β, deg	103.29(2)	104.40(12)	107.80(2)
V, Å^3	2780.1(12)	2560.8(7)	8907(5)
Z	4	4	8
d_{calcd}, g/cm^3	1.957	1.922	1.938
μ, mm^{-1}	5.870	6.357	5.969
θ range, deg	1.75−24.97	1.68−23.47	1.37−23.01
index ranges	$h, \pm k, \pm l$	$h, k, \pm l$	$h, k, \pm l$
no. of reflns obsd	6863	2202	3949
no. of independent reflns $\{I > 2\sigma(I)\}$	4819 [R(int) = 0.0347]	2087 [R(int) = 0.0296]	3851 [R(int) = 0.0274]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data-to-parameter ratio	4819/361	2087/334	3851/588
GOF on F^2	1.002	1.040	1.125
final R indices^a $\{I > 2\sigma(I)\}$	R1 = 0.0322, wR2 = 0.0810	R1 = 0.0549, wR2 = 0.1346	R1 = 0.0532, wR2 = 0.1409
R indices^a (all data)	R1 = 0.0417, wR2 = 0.0854	R1 = 0.0607, wR2 = 0.1390	R1 = 0.0566, wR2 = 0.1437
largest diff peak and hole, e·Å^{-3}	2.344 and −1.183	1.016 and −0.744	1.535 and −0.686

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4\}^{1/2}$, where $w = 1/\{\sigma^2F_o{}^2 + (aP)^2 + bP\}$.

cyanide or NO_2 as a bridging unit.[9] In this study, we obtained three heterometallic coordination polymers with different dimensional structures by inorganic/inorganic self-assembly of copper(II) nitrate and (dmpda)Pt^{II}(isonic)$_2$ or (en)Pt^{II}(nic)$_2$ in aqueous solution. Their structures and magnetic properties are reported here.

Experimental Section

Materials and Physical Measurements. Potassium tetrachloroplatinate from Kojima and 2,2′-dimethyl-1,3-propanediamine (dmpda), ethylenediamine (en), isonicotinic acid (isonicH), nicotinic acid (nicH), and copper(II) nitrate from Aldrich were used as received. The platinum complexes (en)Pt^{II}(nic)$_2$ and (dmpda)Pt^{II}(isonic)$_2$ were prepared by reported methods.[10] Elemental analyses were carried out at the Advanced Chemical Analysis Center, KIST. IR spectra were measured as KBr pellets on an MIDAC 101025 FT-IR spectrometer. Magnetic susceptibility was measured in the temperature range of 5−320 K at 10000 G using an MPMS Quantum Design SQUID magnetometer at the Korea Basic Science Institute. The thermal behavior of the complexes was investigated by thermogravity analysis with TGA/DSC Setaram Scientific & Industrial Equipment (Model Labsys). UV−vis spectra of solutions and solid powders were recorded on a Hewlett-Packard 8453 and Varian Carry 2200 spectrophotometer, respectively. ^{1}H NMR spectra were recorded at 250 MHz using a Bruker 250 MHz NMR spectrometer.

Preparation of $[[(dmpda)Pt(isonic)_2Cu(OH_2)_3](NO_3)_2]_n$ (1). $Cu(NO_3)_2·3H_2O$ (0.45 g, 1.85 mmol) and (dmpda)Pt(isonic)$_2$ (1.00 g, 1.85 mmol) were dissolved in water (10 mL), and acetone (5 mL) was then added to the solution. After 2 weeks, the blue block crystals formed were filtered and washed with cold water and acetone. Yield: 91%. Anal. Calcd for $C_{17}H_{28}N_6O_{13}CuPt·2H_2O$: C, 24.9; H, 3.45; N, 10.26. Found: C, 24.3; H, 3.20; N, 10.37. IR (KBr pellet): ν(COO) = 1636(s), 1384(s). Mp: 208 °C dec.

Preparation of $[[(en)Pt(nic)_2Cu(OH_2)](NO_3)_2]_n$ (2). $Cu(NO_3)_2·3H_2O$ (0.48 g, 2 mmol) and (en)Pt(nic)$_2$ (1.00 g, 2 mmol) were dissolved in water (10 mL), and acetone (5 mL) was added to the solution. After 1 week, the blue thin block crystals formed were filtered and washed with cold water and acetone. Yield: 82%. Anal. Calcd for $C_{14}H_{18}N_6CuPt·2H_2O$: C, 22.7; H, 2.99; N, 11.3. Found: C, 22.8; H, 2.80; N, 10.7. IR (KBr pellet): ν(COO) = 1650(s), 1384(s). Mp: 250 °C dec.

Preparation of $[[((en)Pt(nic)_2)_3Cu_5(OH)_2(OH_2)_6](NO_3)8]_n$ (3). $Cu(NO_3)_2·3H_2O$ (2.4 g, 10 mmol) and (en)Pt(nic)$_2$ (1.00 g, 2 mmol) were dissolved in water (10 mL), and acetone (5 mL) was added to the solution. After 1 week, the green-blue block crystals formed were filtered and washed with cold water and acetone. Yield: 85%. Anal. Calcd for $C_{42}H_{66}N_6O_{46}Cu_5Pt_3·6H_2O$: C, 19.4; H, 3.03; N, 10.8. Found: C, 21.2; H, 3.10; N, 10.0. IR (KBr pellet): ν(COO) = 1626(s), 1392(s). Mp: 228 °C dec.

X-ray Crystallography. All the X-ray data were collected on an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell dimensions were determined from 25 machine-centered reflections. The variation of intensities was monitored by repeated checks of the intensities of three reflections every 1 h during the data collection period. Absorption corrections were applied by an empirical ψ scan method. A direct or Patterson method (SHELXS-86)[11] was employed to locate the platinum atoms. Subsequent cycles of least-squares refinements followed by Fourier syntheses revealed all the other atoms (SHELXL-97).[12] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation using a riding model. All the calculations were carried out using VAX and PC computers. The crystallographic data for the present complexes are summarized in Table 1, and selected bond lengths are listed in Table 2.

---

(8) (a) Subramanian, S.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (b) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 1677. (c) Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W.-S. *J. Chem. Soc., Dalton Trans.* **1997**, 913.

(9) (a) Miasaka, H.; Matsumoto, N.; Gallo, N. R. E. Floriani, C. *Inorg. Chem.* **1997**, *36*, 670. (b) Ohba, M.; Fukita, N.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1997**, 1733. (c) Kahn, O.; Bakalbasis, E.; Mathoniere, C.; Hagiwara, M.; Katsumata, K.; Ouahab, L. *Inorg. Chem.* **1997**, *36*, 1530.

(10) Song, R.; Kim, K. M.; Sohn, Y. S. *Inorg. Chim. Acta* **1999**, *292*, 238.

(11) Sheldrick, G. M. *SHELXS-86: A Program for Structure Determination*; University of Göttingen: Göttingen, Germany, 1986.

(12) Sheldrick, G. M. *SHELXL-97: A Program for Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**[a]

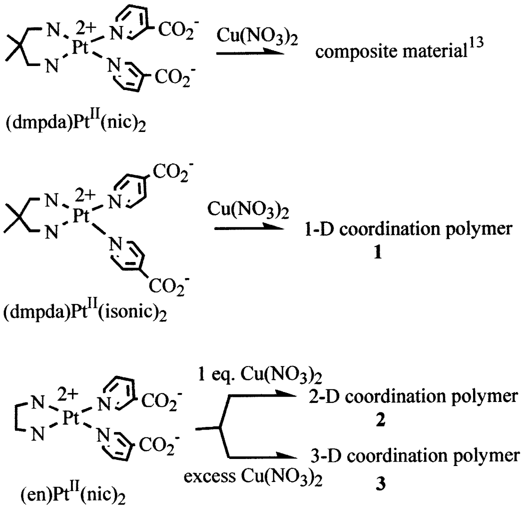
		1	
Cu−O(3)	1.914(4)	Cu−O(1)#1	1.926(4)
Cu−O(6)	1.977(5)	Cu−O(5)	1.988(4)
Cu−O(7)	2.305(4)		
O(3)−Cu−O(6)	90.72(18)	O(1)#1−Cu−O(6)	91.74(19)
O(3)−Cu−O(5)	89.31(18)	O(1)#1−Cu−O(5)	87.78(18)
O(3)−Cu−O(7)	87.39(16)	O(5)−Cu−O(7)	98.79(17)
		2	
Cu−O(2)	1.953(15)	Cu−O(3)#2	1.950(15)
Cu−O(1)#3	1.965(13)	Cu−O(4)#4	1.997(16)
Cu−O(5)	2.149(16)	Cu−Cu#3	2.660(5)
O(3)#2−Cu−O(2)	88.7(7)	O(3)#2−Cu−O(1)#3	90.1(7)
O(2)−Cu−O(4)#4	88.1(7)	O(2)−Cu−O(5)	94.8(7)
O(1)#3−Cu−O(5)	98.6(6)	O(4)#4−Cu−O(5)	95.9(6)
O(2)−Cu−Cu#3	82.6(5)	O(5)−Cu−Cu#3	177.4(5)
		3	
Cu(1)−O(7)	1.954(10)	Cu(1)−O(1)	1.996(10)
Cu(1)−O(5)	2.315(11)	Cu(2)−O(9)	1.968(12)
Cu(2)−O(7)	1.961(10)	Cu(2)−O(2)	1.976(10)
Cu(2)−O(8)	2.399(13)	Cu(2)−O(3)#5	1.961(11)
Cu(3)−O(4)#5	1.935(12)	Cu(3)−O(10)	1.947(13)
Cu(3)−O(11)	2.315(12)	Cu(3)−O(6)	1.927(11)
Cu(3)−O(7)	1.954(10)		
O(7)−Cu(1)−O(1)	90.9(4)	O(7)−Cu(1)−O(5)	89.5(4)
O(3)#5−Cu(2)−O(7)	95.9(5)	O(3)#5−Cu(2)−O(9)	87.8(5)
O(7)−Cu(2)−O(8)	85.7(5)	O(9)−Cu(2)−O(8)	92.0(5)
O(2)−Cu(2)−O(8)	85.2(4)	O(6)−Cu(3)−O(10)	86.3(6)
O(4)#5−Cu(3)−O(10)	86.2(6)	O(6)−Cu(3)−O(7)	92.1(5)
O(4)#5−Cu(3)−O(7)	95.4(5)	O(4)#5−Cu(3)−O(11)	88.6(5)
O(10)−Cu(3)−O(11)	92.8(6)	O(7)−Cu(3)−O(11)	90.9(4)

[a] Symmetry transformations #1−5 are recorded in the captions of Figure 1−3.

Results and Discussion

Synthesis and Properties. Three different dimensional heterometallic coordination polymers were obtained by reaction of copper(II) nitrate with zwitterionic platinum complexes (dmpda)Pt^{II}(isonic)$_2$ and (en)Pt^{II}(nic)$_2$ in contrast to the composite material [(dmpda)Pt^{II}(nic)$_2$][Cu(OH$_2$)$_5$]·2NO$_3$·5H$_2$O obtained from the reaction of copper(II) nitrate with (dmpda)Pt^{II}(nic)$_2$ in our previous study[13] (Scheme 1). The crystals of the present coordination polymers were found to lose their crystallinity when exposed to air presumably due to loss of water of crystallization and decompose in the temperature range of 208−250 °C. The crystals are slightly soluble in water but insoluble in most common organic solvents. Their UV−vis spectra in aqueous solution showed maximum absorbances (λ_{max}) in the region of 770−790 nm, corresponding to that[14] of the hydrated Cu^{2+} ion. The chemical shifts in the ^{1}H NMR spectra of the crystals in D$_2$O solution are almost the same as those of the discrete platinum complexes. Such results indicate that the chemical interactions between the platinum complexes and copper ions through carboxylate−Cu bonds are weak or absent in aqueous solution. The solid electronic reflectance spectra of these coordination polymers showed λ_{max} values in the region of 725−750 nm, while the previously reported composite material,[13] containing only hydrated copper ion in the solid state, showed λ_{max} at 814 nm, which implies that the copper ions in the crystals obtained in the present study are coordinated by pyridinecarboxylates in the solid state.[15] As a matter of fact, it has been shown by X-ray crystallographic studies that the present coordination polymers have a variety of Cu−carboxylate coordination bonds, yielding different dimensional structures. The crystals obtained by reaction of equimolar copper(II) nitrate with (dmpda)Pt(isonic)$_2$ and (en)Pt(nic)$_2$ were found to be a zigzag-type 1-D coordination polymer (**1**) and a 2-D coordination polymer (**2**), respectively, and the crystals obtained from (en)Pt(nic)$_2$ and excess copper(II) nitrate were a 3-D coordination polymer (**3**).

Scheme 1. Self-Assembly of (Diamine)Pt(pyridinecarboxylates)$_2$ with Copper(II) Nitrate



Crystal Structure of 1. The extended and local molecular structures of crystal **1** are shown in parts a and b, respectively, of Figure 1. The polymer has a repeated zigzag unit in which the Cu−Pt−Cu angle is 64.9°. One copper atom connects two (dmpda)Pt^{II}(isonic)$_2$ moieties through monodentate coordination by the carboxylate group of the isonicotinate ligand. The carboxylate oxygen atoms O(1) and O(3) are separated from the copper atom by 1.926(4) and 1.914(4) Å, respectively. Three water molecules are also bound to the copper atom. The axial water molecule (O(7)) is separated from the copper atom by 2.305(4) Å. The coordination geometry around the copper atom is square pyramidal, as is typically observed in other copper compounds.[16] The structural properties of the (dmpda)Pt^{II}(isonic)$_2$ moiety are similar to those[10] previously reported. One linear zigzag-type polymer chain is fitted to the neighboring one via hydrogen-bonding interactions between N(3)---O(7) and N(4)---O(4), whose distances are 2.99 and 2.87 Å, respectively.

Crystal Structure of 2. The dimeric copper unit depicted in Figure 2a is observed in the crystal structure of **2**: Four carboxylate groups from four (en)Pt^{II}(nic)$_2$ moieties bridge two copper atoms separated by 2.660(5) Å. A water molecule

---

(13) Song, R.; Kim, K. M.; Sohn, Y. S. *Inorg. Chim. Acta* **2000**, *304*, 156.
(14) Bjerrum, J.; Ballhausen, C. J.; Jørgensen, C. K. *Acta Chem. Scand.* **1954**, *8*, 1275.
(15) Graddon, D. P. J. *Inorg. Nucl. Chem.* **1958**, *7*, 93.
(16) King, R. B. *Encyclopedia of Inorganic Chemistry*; John Willy & Sons: Chichester, U.K., 1994; Vol. 2.

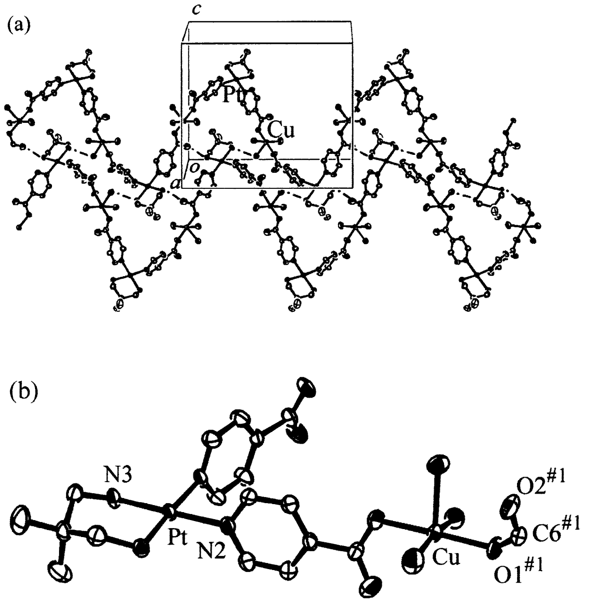


Figure 1. Structures of **1**. (a) An extended structure. Dashed lines indicate intermolecular hydrogen bonds. (b) Structure around Pt and Cu atoms. Symmetry transformation: #1, $0.5 - x$, $0.5 - y$, $2.5 - z$.

(O(5)) is coordinated to a copper atom of the dimeric unit at the axial position with a bond distance of 2.149(16) Å. Distances from copper to carboxylate oxygens of nicotinate vary from 1.950(15) to 1.997(16) Å. The structural features of the dimeric copper unit are similar to those of the dimeric copper(II) acetate,[17] where Cu---Cu separation was observed to be 2.616(1) Å. Four such dimeric units and four (en)Pt^{II}(nic)$_2$ moieties constitute a macrocyclic ring as shown in Figure 2b. This ring is twisted, with the shortest distance between two platinum atoms being 5.25 Å and the longest distance being 21.07 Å. There are two crystallographically equivalent nitrate anions inside this ring, which are not included in the figure. Infinite conjunctions of the macrocyclic ring complete a 2-D network, which has a waved surface, and the distance between two waves corresponds to 1.37 nm (Figure 2c).

Crystal Structure of 3. The unique pentanuclear copper unit found in polymer **3** is shown in Figure 3a. Six carboxylate groups, eight water molecules, and two hydroxide ions are involved in binding of the five copper(II) ions. This unit has an inversion center at the atom Cu(1), and the five copper atoms lie on the same plane. The distances of Cu(1)−O(1), Cu(1)−O(5), and Cu(1)−O(7) are 1.996(10), 2.315(11), and 1.954(10) Å, respectively. The coordination polyhedron around Cu(1) can be defined as being a distorted octahedron, which is rarely found in the copper compounds with all oxygen donor ligands. The coordination geometry around Cu(2) and Cu(3) is a square pyramid, as is commonly found in other copper complexes. The atom O(7) bridges the three copper atoms in a μ^3 manner and is assessed to be a hydroxide ion (OH^-) by considering the number of nitrate anions observed in the X-ray crystallographic study. There are two crystallographically different (en)Pt(nic)$_2$ moieties in the crystal structure of **3**: One moiety bearing platinum atom Pt(1) constitutes the ladder-type polymer shown in Figure 3b, and the other moiety bearing platinum atom Pt(2) connects two ladder-type polymers as shown in Figure 3c. Among the six carboxylate groups involved in binding of the pentanuclear copper unit, the carboxylate groups labeled O(1), O(2), C(14), O(3), O(4), and C(8) are from four (en)Pt^{II}(nic)$_2$ moieties bearing Pt(1), while the carboxylate groups labeled by O(5), O(6), and C(21) are from two (en)Pt^{II}(nic)$_2$ moieties bearing Pt(2). If we exclude (en)Pt^{II}(nic)$_2$ moieties bearing Pt(2) in the crystal structure of **3**, we observe the ladder-type coordination polymer as shown in Figure 3b, in which the pentanuclear unit looks like a rung. The size of the rung is approximately 5.2 Å, and the distance between the two rungs is 13.5 Å. When the (en)Pt^{II}(nic)$_2$ moieties bearing Pt(2) are included, the three-dimensional structure of crystal **3** is completed by a backbone structure

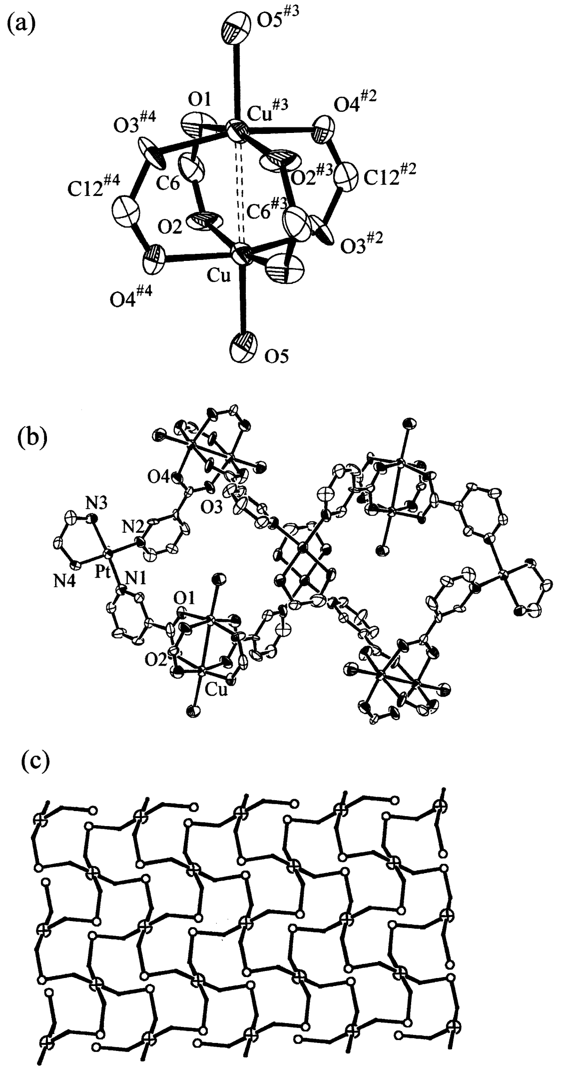


Figure 2. Local structures of **2**. (a) Structure of the dimeric copper unit. Symmetry transformations: #2, x, $1.5 - y$, $0.5 + z$; #3, $1 - x$, $1 - y$, $2 - z$; #4, $1 - x$, $-0.5 + y$, $1.5 - z$. (b) Structure of the macrocyclic ring, with several atoms in the asymmetric unit labeled. (c) Extended backbone structure of **2** drawn using only the coordinates of Pt, C(6), and C(12) and the inversion center of the dimeric copper unit. The structure is viewed along the *a* axis.

---

[17] Meester, P. D.; Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1973**, 2575.

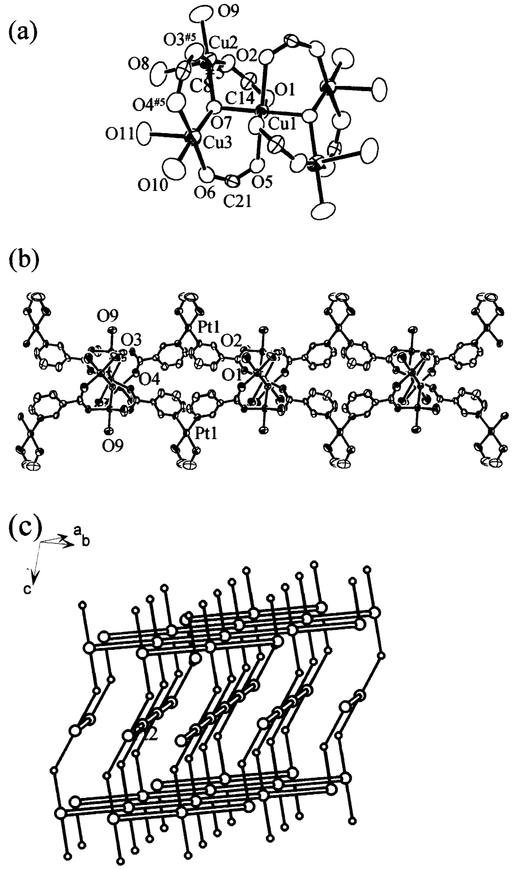


Figure 3. Local structures of **3**. (a) Pentanuclear copper unit. The inversion center lies at the Cu(1) atom. Symmetry transformation for the atoms C(8), O(3), and O(4): #5, 0.5 + *x*, 0.5 + *y*, *z*. (b) A ladder-type coordination polymer. The (en)Pt(nic)$_2$ moieties with Pt(2) labeling at the platinum atoms are omitted. (c) Backbone structure of **3**. A large circle and a small circle indicate the pentanuclear unit and Pt(2), respectively. The parallel lines indicate the ladder-type polymer shown in (b). A solid line indicates nicotinate, which is N-coordinated to Pt(2) and O-coordinated to the pentanuclear copper unit.

depicted in Figure 3c, whose topology is similar to the 3D network of $CdSO_4$ in the literature.[18] In this structure, the ladder-type polymers of Figure 3b run in either of two directions, [110] or [$\bar{1}$10], and (en)Pt^{II}(nic)$_2$ moieties with the labeling of Pt(2) link the two ladder-type polymers running in the two different directions by carboxylate coordination to the pentanuclear copper units.

Ligand Effect on the Molecular Structure. It is interesting that structural change either of the amine or pyridinecarboxylate ligand resulted in completely different products as shown in Scheme 1. We found from the structural analysis of (dmpda)Pt(isonic)$_2$ and (dmpda)Pt(nic)$_2$ that the two methyl groups of the dmpda ligand lie between the two anionic ligands as shown in Figure 4.[10,13] The distances from the methyl groups to the carbon atoms of the pyridine ring range from 3.8 to 4.0 Å, which may accommodate hydrophobic interactions.[19] Such a disposition of the dmpda ligand is conserved in the crystal structures of the 1-D coordination polymer **1** and the composite material [(dmpda)Pt^{II}(nic)$_2$][Cu(OH$_2$)$_5$]·2NO$_3$·5H$_2$O.[13] In the crystal structure of the composite material, strong hydrogen bonding between amine hydrogens and nicotinate oxygens was also observed in addition to the above-mentioned hydrophobic interactions. Such dual intermolecular interactions seemed to inhibit the formation of coordination bonds between the nicotinate oxygens and copper(II) ion. However, the crystal structure of (dmpda)Pt(isonic)$_2$ shows no such hydrogen bonding, but the hydrophobic interaction between the methyl groups of dmpda and the isonicotinate ligand seems to be conserved to form the coordination polymer **1**. In the cases of crystals **2** and **3** bearing en instead of dmpda, close interaction between ethylene groups and pyridine moieties seems unfavorable, which is presumed to be a reason completely different crystals were obtained. It may be concluded that the hydrophobic interaction between the amine methyl groups and pyridinecarboxylate ligands and the hydrogen-bonding interaction are important factors in determining the final structure of the products resulting from the reaction of copper nitrate and (diamine)Pt(pyridinecarboxylates)$_2$.

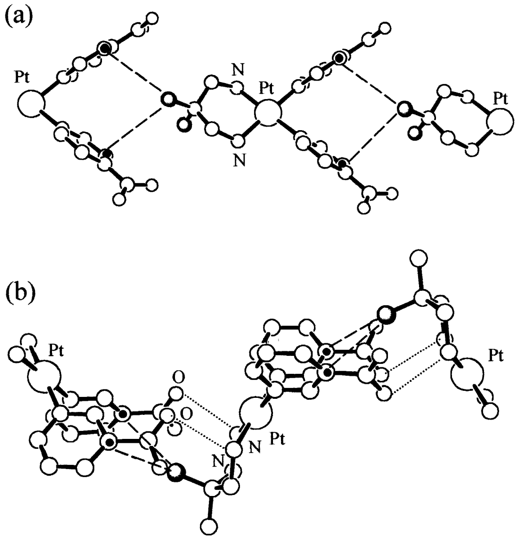


Figure 4. Intermolecular interactions observed in the crystal structures of (a) (dmpda)Pt(isonic)$_2$ and (b) (dmpda)Pt(nic)$_2$. The dashed lines indicate the close distances in the range of 3.8−4.0 Å between the methyl groups (shaded circle) and the pyridine carbons (marked by a black dot). The dotted lines indicate hydrogen bond distances in the range of 2.9−3.0 Å.

Magnetic Properties. The magnetic susceptibility of the three coordination polymers **1**−**3** was measured in the temperature range of 4−320 K. The magnetic behavior of the 1-D polymer obeys the Curie law $\chi = C/T$ with the Curie constant $C = 0.463$ emu K mol^{-1}, which corresponds to a spin-only magnetic system with $g = 2.22$ and $S = 1/2$. The temperature-dependent magnetic susceptibilities of crystal **2** are plotted in Figure 5a, and the temperature-dependent curve was found to be fitted best to the Bleaney−Bowers equation[20] $\chi_M = (2Ng^2\mu B^2/3kT)[1 + (1/3)\exp(-2J/kT)]^{-1}$ at $g = 1.67$ and $-2J/k = 462$ K. The magnetic susceptibility of this 2-D polymer passes through the maximum at room temperature

---

(18) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solution Chem.* **2000**, *152*, 3.

(19) Lee, Y.-A.; Jung, O.-S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3868.

(20) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

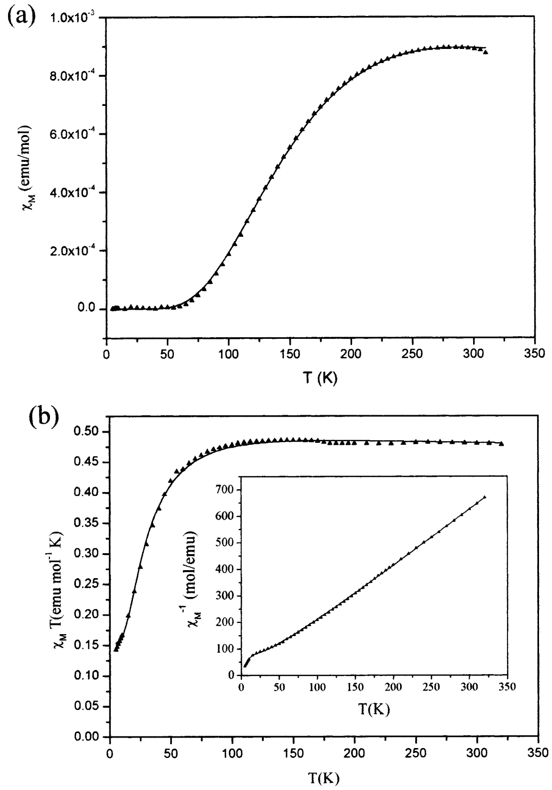
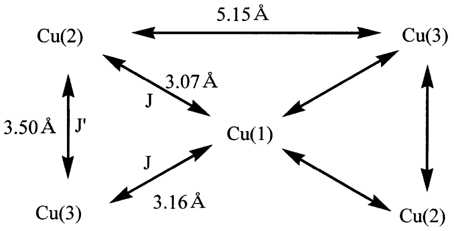


Figure 5. (a) χ_M vs T for crystal **2**. (b) $\chi_M T$ and $\chi_M^{-1}T$ vs T for crystal **3**. ▲: experimental data. Solid line: calculated curve.

(T_{max} = 285 K). Such magnetic properties of crystal **2** are quite similar to those[21] of the dimeric copper acetate $[Cu(OAc)_2(OH_2)]_2$, in which the values of $-2J/k$ and T_{max} were reported to be 480 and 255 K, respectively.

In the case of crystal **3**, the pentanuclear copper cluster can be approximately reduced to a trinuclear system with two coupling constants of J and J' when the magnetic interactions between long-distant metal pairs are excluded. The temperature-dependent curve of the magnetism of crystal **3** is fitted with an equation[22] that describes the magnetism of such a trinuclear system, $\chi_M = (N\mu_B^2/3kT)(g^2/4)[(e^{-A+B} + e^{-A-B} + 10e^{A})/(e^{-A+B} + e^{-A-B} + 2e^{A})]$ ($A = (2J + J')/2kT$ and $B = (J - J')/kT$), best at $g = 2.22$, $J/k = -16$ K, and $J'/k = 90$ K (Figure 5b). The fitted values imply that antiferromagnetic and ferromagnetic couplings coexist in the system.



Conclusion

The crystals grown in aqueous solution by inorganic/inorganic self-assembly of (diamine)Pt^{II}(pyridinecarboxylates)$_2$ with copper(II) nitrate exhibit different structural features depending on the structures of the amine and pyridinecarboxylate ligands as well as the mole ratio of the reactants. Even though the resultant structural variety cannot be explained clearly, the disposition of the methyl groups of the dmpda ligand between the two pyridine rings is suggested to be an important factor that determines the structure of the self-assembled products. The crystal engineering method used in this study has been proved to be efficient for preparing heterometallic coordination polymers. The polymeric nature of the crystals was observed to be lost when they were dissolved in aqueous solution. The magnetic properties of crystals **1**−**3** were different depending on the local structure around the copper(II) ion, but magnetic coupling through platinum complexes was not detected. The coexistence of antiferromagnetic and ferromagnetic couplings was observed in the pentanuclear copper cluster in crystal **3**.

Acknowledgment. This research was supported by the Basic Research Program of the Korea Science & Engineering Foundation (Grant R05-2000-0008) and the Ministry of Science and Technology in Korea.

Supporting Information Available: X-ray crystallographic files for complexes **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0204777

---

[21] Figgis, B. N. *J. Chem. Soc.* **1956**, 3837.

[22] Sinn, E. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 193.