Anion-Controlled Copper(II) Coordination Polymers Based on Angular Dipyridyl Ligand

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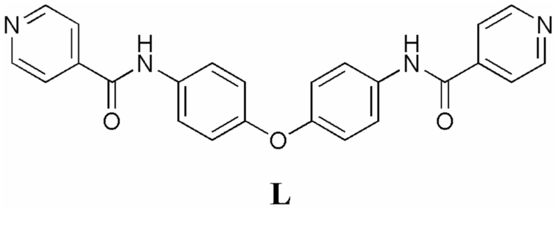
An increasing interest has been directed toward the study of new metal-organic frameworks due to potential applications.[1-4] In this case, the particular product formed depends on a delicate balance between alternative conformations of the organic ligands and on the nature of the metals and anions as well as solvent molecules employed. Topologically, an angular bidentate ligand can form a discrete dimer, a 1D chain, and an infinite loop-chain, etc.[5] On the other hand, the use of longer ligands tends to lead the construction of frameworks with interpenetrating structure, which hinders the formation of the useful void space.[6-8]

In our efforts to investigate the factors for the control of the self-assembly of such frameworks, dipyridyl-based ligands separated by a phenyl amide spacer *N*,*N'*-bis(4-pyridylcarbonyl)-4,4'-diaminodiphenyl ether (**L**) has attracted our attention in connection with the coordination affinity and structural control of discrete or divergent coordination networks upon metal complexation under appropriate conditions.[9,10] Li *et al.*[11] reported the structure of $M_2\mathbf{L}_2$-type (M = Zn and Cd) molecular squares. Recently, we have reported a discrete dimer $[Co_2(\mathbf{L})_2(NO_3)_2(H_2O)_4(CH_3OH)_2](NO_3)_2\cdot C_2H_5OC_2H_5$, a 1D loop-chain $\{[Co(\mathbf{L})_2(H_2O)_2](PF_6)_2(H_2O)\}_n$, and an interpenetrating 3D polymeric network $\{[Co_2(\mathbf{L})_2(NO_3)_2]\cdot(C_2H_5OC_2H_5)_2\cdot(CH_3)_2SO\cdot(H_2O)\}_n$ with spacious nano-sized channels.[9,10] The results clearly indicate the important role that the coordination ability of the counteranions of cobalt(II) can play.

As a result of continuing interest, we have further carried out the self-assembly of **L** with the copper(II) salts keeping in mind that a more subtle effect affecting the final topological arrangement may arise from anion control or regulation.[12-14] In this paper, we report two distinctive copper(II) complexes $\{[Cu(\mathbf{L})(NO_3)_2(CH_3OH)](CH_3OH)\}_n$ (**1**) and $[Cu(\mathbf{L})_2(PF_6)_2]_n$ (**2**), which are varied with the anions used.



L

The ligand **L** was prepared with the method reported previously.[9,11] Two complexes **1** and **2** were prepared from the reactions of **L** with copper(II) salts (**1**: NO_3^- and **2**: PF_6^- forms) as follows. In both cases, copper(II) nitrate in chloroform-methanol mixture (1 : 1 v/v) was layered onto a chloroform-methanol mixture (1 : 1 v/v) solution of **L** after layering with 3-4 drops of water. In case of **2**, excess amount of ammonium haxafluorophosphate was added to the above reaction mixture. In each case, green (**1**) and dark-blue (**2**) crystalline complexes suitable for X-ray analysis were formed after slow evaporation at room temperature. Isolated yields were greater than 20%. $[Cu(\mathbf{L})_2(PF_6)_2]_n$ (**2**) Anal. Calcd. for $C_{48}H_{36}O_6N_8P_2F_{12}Cu$, $[Cu(\mathbf{L})_2(PF_6)_2]$: C 49.09, H 3.09, N 9.54. Found C 49.04, H 3.45, N 9.69%. Due to the slow loss of solvent molecules, no satisfactory elemental analysis result for **1** was available.

The crystallographic analysis reveals that **1** is a 1D polymeric chain of formula $\{[Cu(\mathbf{L})(NO_3)_2(CH_3OH)](CH_3OH)\}_n$ (Figure 1). The asymmetric unit contains one copper atom, two nitrate ions, one ligand, and two methanol molecules. In the crystal, one ligand and one copper atom are interconnected alternately to form an infinite -**L**-Cu-**L**-Cu- chain. The copper is bound to two pyridyl N donors from two different ligands, two monodentate nitrate ions and one methanol molecule such that the overall coordination geometry about the copper atom is five-coordinate. The coordination geometry can be described as a distorted trigonal bipyramid. The displacement of the central copper atom from the average equatorial plane is only 0.021(3) Å. Around Cu1 atom, for example, N1, O10 and N4 atoms are forming the equatorial trigonal plane and two O atoms from the monodentate nitrate ions are occupying the axial position (O4-Cu1-O7 167.9(3)°). The bond angle between the copper and two N donors of two pyridine groups is 158.4(3)°, resulting in a sinusoidal chain motif. Of further interest, these infinite chains are arranged in a parallel fashion. Two adjacent chains (A and B) interact pair-wise in a “head-to-tail” mode through the H-bonds (between amide C=O and NH, C=O···N 2.947 Å) and π-π stacking (4.063 Å).

To examine the role of anions in the formation of the coordination polymers, the reaction was repeated with $Cu(PF_6)_2$ instead of $Cu(NO_3)_2$. The structure of complex **2** is more complicate and interesting. Here, **2** was revealed as a

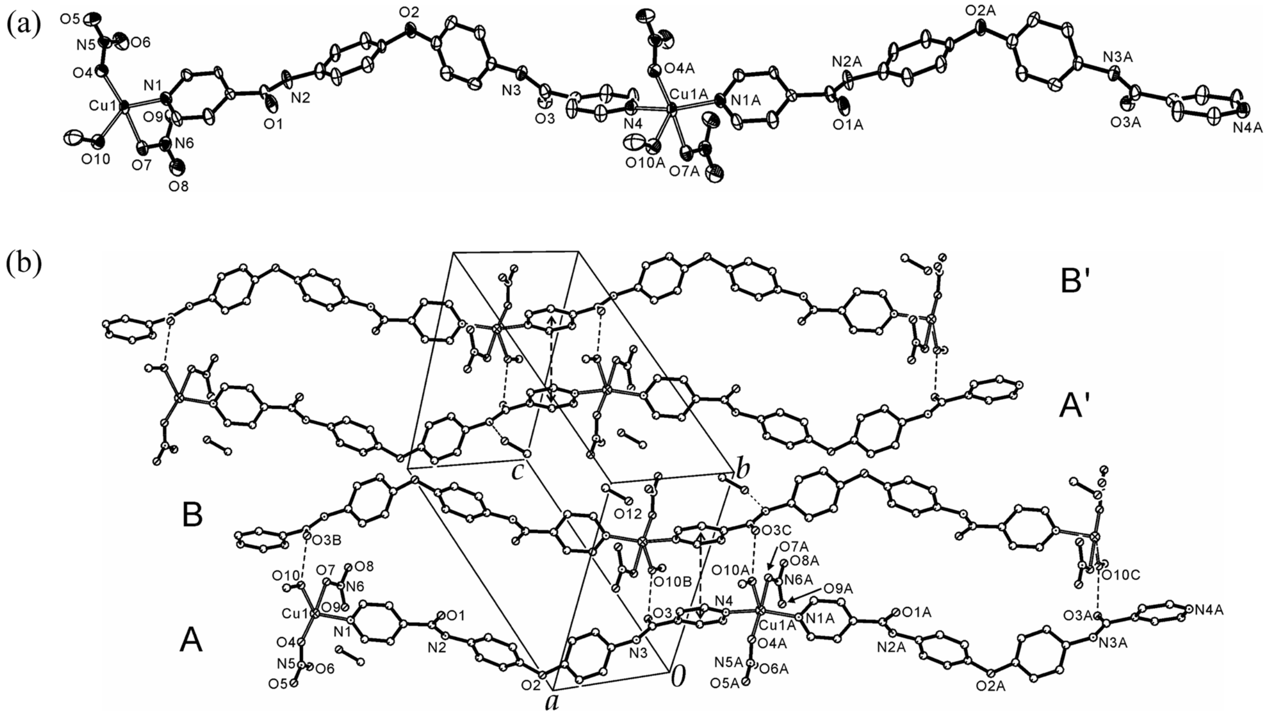


Figure 1. (a) Coordination environment of **1**, $\{[Cu(\mathbf{L})(NO_3)_2(CH_3OH)](CH_3OH)\}_n$ and (b) packing diagram of **1** showing interchain interactions (H-bonds: dashed lines and π-π stacking: arrowed dashed lines). Selected bond lengths (Å) and bond angles (°): Cu1-O7 1.989(6), Cu1-O4 2.029(6), Cu1-N4A 2.002(7), Cu1-O10 2.271(6), Cu1-N1 2.013(6), O7-Cu1-N4A 91.4(3), N1-Cu1-O10 100.9(3), O7-Cu1-N1 90.5(3), O4-Cu1-O10 87.2(2), N4A-Cu1-N1 158.4(3), O7-Cu1-O4 167.9(3), N4A-Cu1-O4 92.5(3), N1-Cu1-O4 90.1(3), O7-Cu1-O10 80.8(2), N(4)A-Cu(1)-O(10) 100.7(3) [Symmetry codes: A) $x + 2, y - 1, z + 1$; B) $-x + 2, -y, -z + 1$; c) $-x, -y + 1, -z$]

2D polymeric array of formula $[Cu(\mathbf{L})_2(PF_6)_2]_n$, in which the 1D loop-chains formed are interpenetrated (Figure 2). The gross geometry of the resulting 2D architecture can be described as an infinite square-grid. An asymmetric unit of **2** consists of one copper atom, half molecule of ligand and half of PF_6^- ion. Coordination geometry of the copper atom is distorted octahedral. Each copper atom is coordinated by four pyridyl nitrogen donors of four different ligands in an equatorial plane. Two PF_6^- ions in *trans*-geometry coordinate weakly to the metal center. The bond distance of Cu-F [2.525(7) Å] falls on the longer end of those (2.3-2.6 Å) in literature.[15,16] Two adjacent copper atoms are doubly bridged by two ligands, forming a 1D loop-chain. Two coordinating PF_6^- ions locate in each loop cavity. As mentioned, the loop-chains arranged in two directions are further interlocked, leading to the formation of a 2D interwoven square-grid layer structure. The 2D layer is expanded in the crystallographic *bc*-plane. The interwoven structure is also stabilized by H-bonds between amide C=O and NH from two different loop-chains (dashed lines in Figure 2b).

Comparing the structures between **1** and **2** afforded a good case for the anion effect on the frameworks of coordination polymers. The coordinating ability, size and shape of anions are primary reasons behind the differences in the structures of these two copper(II) complexes. The smaller NO_3^- ion in **1** possesses stronger coordination or donor affinity than PF_6^- ion, and serves as linkage to bridge the 1D chain by the axial N(py)-Cu-N(py) bond because the stronger affinity of two NO_3^- ions toward Cu(II) center prevents the approach of the pyridyl N donors to form a higher dimensional network. In case of **2**, the preference of 2D layer structure is due to the weaker affinity of PF_6^- ion toward Cu(II) center, allowing the approach of the pyridyl N donors to form a framework with higher dimension.

Experimental Section

General. All commercial reagents including solvents were analytical reagent grade. Microanalysis was performed by Elementar Analysensysteme Vario EL in KBSI (Daegu).

X-ray crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated MoK$_\alpha$ (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The frame data were processed to give structure factors using the program SAINT.[17] The absorption corrections were based on multiple and symmetry-equivalent reflections in the data sets using SADABS program for **1** and **2**.[18] The structure was solved by a direct method and refined by full matrix least squares against F^2, for all data using SHELXTL software.[19] All non-H atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data is given in Table 1.

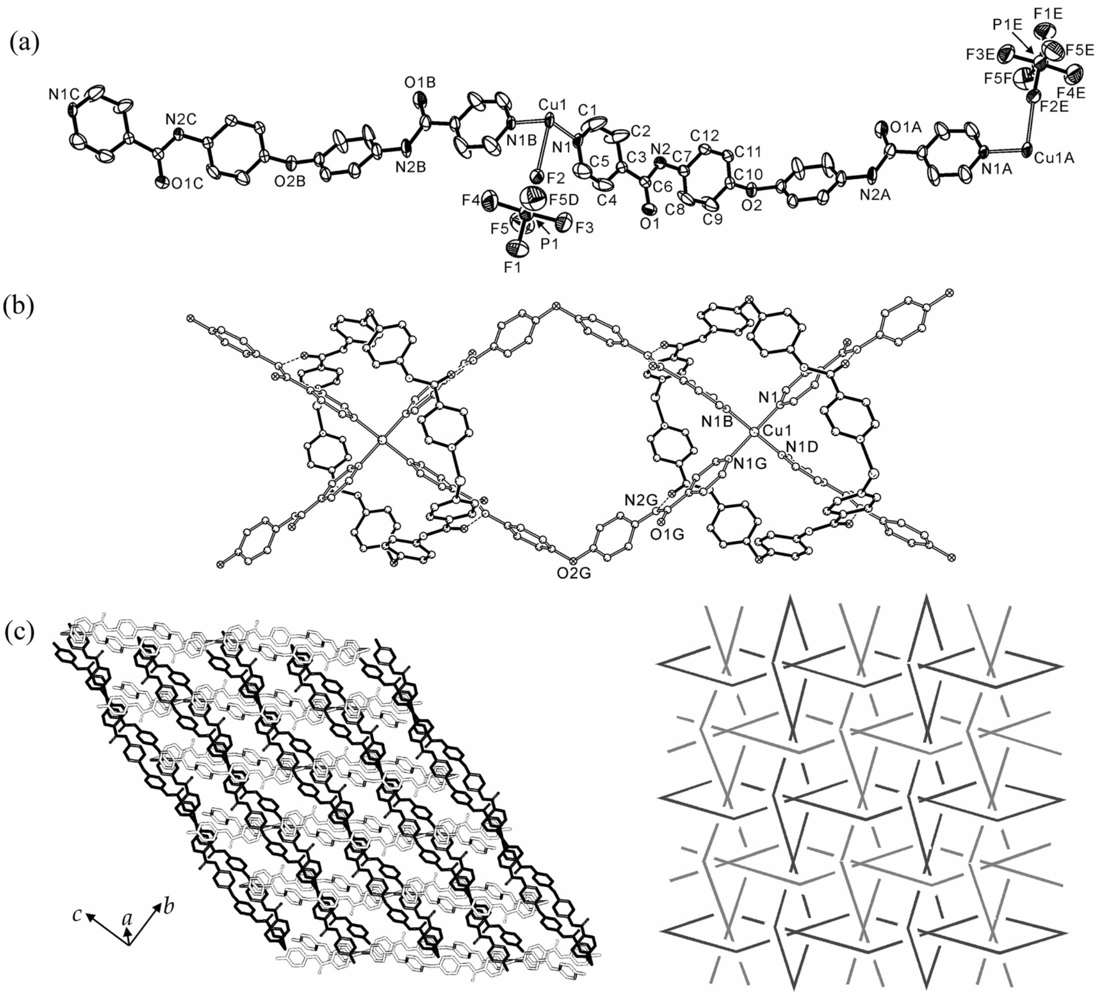


Figure 2. (a) Coordination environment of **2**, $[Cu(\mathbf{L})_2(PF_6)_2]_n$, (b) one loop unit consisting of two ligands and two copper atoms in **2** (The coordinated PF_6^- ions and H atoms were omitted for clarity.) and (c) packing diagram (left) and its schematic representation (right) of **2** showing interpenetrated 2D network. Selected bond lengths (Å) and bond angles (°): Cu1-N1 2.006(7), Cu1-F2 2.525(7), N1-Cu1-N1B 92.0(4), N1-Cu1-N1G 180.0(4), N1-Cu1-N1D 88.0(4), N1B-Cu1-N1G 88.0(4), N1B-Cu1-N1D 180.0(4), N1G-Cu1-N1D 92.0(4). [Symmetry codes: A) $x, -y, -z + 1$; B) $x, -y + 1, -z$; C) $x, y + 1, z - 1$; D) $-x, y, z$; E) $-x, -y, -z + 1$; F) $x, y, -z + 1$; G) $-x, -y + 1, -z$]

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

	$[Cu(\mathbf{L})(NO_3)_2(CH_3OH)]$ (CH_3OH) (**1**)	$[Cu(\mathbf{L})(PF_6)]$ (**2**)
Empirical formula	$C_{26}H_{26}CuN_6O_{11}$	$C_{48}H_{36}CuF_{12}N_8O_6P_2$
Formula weight	662.07	1174.33
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1	*Cmca*
a / Å	7.799(3)	29.021(13)
b / Å	14.077(6)	9.157(6)
c / Å	14.540(6)	18.413(8)
α / °	70.779(9)	
β / °	77.451(8)	
γ / °	82.088(9)	
V / Å^3	1467.6(11)	4893(4)
T / K	298(2)	298(2)
μ (Mo-K$_\alpha$)/mm^{-1}	0.814	0.617
Reflection collected	9538	15039
Independent reflections	6695	3069
Final R_1, wR_2 indices [$I > 2\sigma(I)$]	0.0882, 0.1391	0.0963, 0.2539
R_1, wR_2 [all data]	0.3090, 0.2098	0.2893, 0.3724

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Supplementary data. CCDC 615413 (for **1**) and 615414 (for **2**) contain the supplementary crystallographic data. These data can be obtained free of charge *via* www.ccdc.ac.uk/data_request/cif, by emailing data request@ccdc.cam.ac.kr, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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