Structures and Photoluminescence Properties of 2-Dimensional Copper(I)-Halide Complexes Constructed by Rhomboid Cu_2X_2 (X = I and Br) Units and Dipyridyl Ligand

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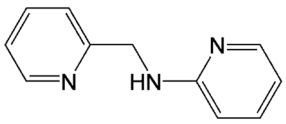
The structural and photophysical properties of transition-metal complexes have been attracted an increasing attention because of their chemically-interesting structural features as well as their potential applications such as sensors and light emitting diodes.[1-5] Among the coinage metal ions with the d^{10} electron configuration, copper(I) ion has been spot-lighted as a good candidate in synthesis of complexes with intriguing structures as well as photophysical properties. Because copper(I) complexes show the unusual geometries and stoichiometries depending on synthetic conditions.[2-4] Especiallly, copper(I)-halide complexes are well-known as blue to red luminescence materials.[2,4] Recently, we have focused on the development of luminescence copper(I) coordination polymers with dipyridyl or dithioether ligands. During our investigation on copper(I) coordination polymers, the structures and photophysical properties for copper(I)-halide complexes with dithioether ligands have been reported.[2a,5] However, the relationship between the structure and photoluminescence property for copper(I) complexes still remains as research topic to be examined. Herein, we report structures, thermal behaviors and photoluminescence properties of two-dimensional coordination polymers constructed by rhomboid Cu_2X_2 (X = I for **1** and Br for **2**) unit and dipyridyl ligand.



L

Dipyridyl ligand **L** was synthesized by the reaction of 2-aminopyridine and 2-pyridinecarboxaldehyde.[9] The reddish brown crystals of **1** and **2** were obtained by slow diffusion of a MeCN solution of CuX (X = I and Br) layered with a blank MeCN solvent as buffer zone and a MeCN solution of **L**. Single-crystal X-ray diffraction studies reveal that **1** and **2** are isostructures and can be described as 2D brick-wall type complexes with polymeric array of formula $[CuX(\mathbf{L})]_n$, confirmed by elemental analysis.

In each crystal structure of **1** and **2**, the asymmetric unit consists of a copper and a halide atom per one **L**. As shown in Figure 1, each copper(I) atom is coordinated in distorted tetrahedral geometry by two iodide atoms and two nitrogen atoms from two different ligands: the tetrahedral angles are in the range of 104.88(3)-115.84(13)° for **1** and 102.64(4)-115.90(17)° for **2**. Each **L** bridges two copper ions *via* two nitrogen atoms of pyridyl group to form an one-dimensional -(Cu-**L**)$_n$- chain, and the halide ions connect these chains in μ-bridging mode *via* symmetry-related copper atoms to generate an undulant 2D network. The topology of 2-D network is a brick-wall type (Fig. 2a). A single brick unit contains four asymmetric units where each ligand is inter-connected with the Cu-(μ-X)$_2$-Cu nodes alternately. The Cu_2X_2 unit adopts the slightly distorted rhomboid shape because of uneven Cu-X (X = I and Br) bond distances (2.6514(8) and 2.7074(8) Å for **1** and 2.5134(13) and 2.5495(12) Å for **2**). However, the rhomboid Cu_2X_2 unit is strictly planar due to the inversion center located on the center of Cu_2X_2 unit, and Cu···Cu separations are 3.266 Å for **1** and 3.164 Å for **2**. These separation distances are agreement with the long end of the range for other complexes with Cu_2X_2 units (2.566-3.452 Å).[3] Within the brick unit, weak π-π interactions exist between two parallel

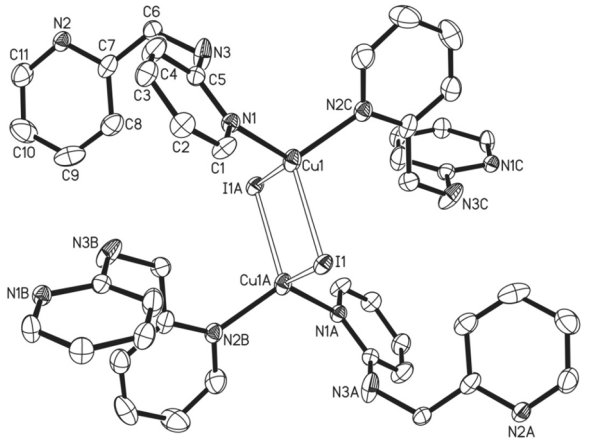


Figure 1. Ortep representation showing the coordination environments of metal centers in **1**, $[CuI(\mathbf{L})]_n$. Hydrogen atoms and disorder parts are omitted for clarity. [Symmetric codes: A) $-x+1, -y+1, -z+1$; B) $x, -y+0.5, z+0.5$; C) $-x+1, y+0.5, -z+0.5$]

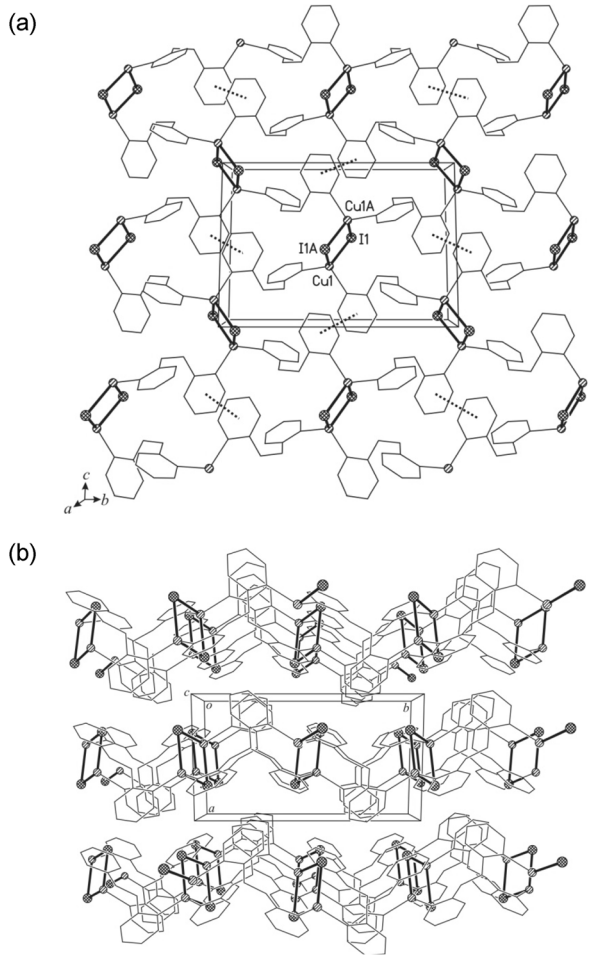


Figure 2. Perspective view of **1**: (a) the structure of one layer and (b) the packing structure of undulant 2D layers. Hydrogen atoms are omitted for clarity. [Symmetric codes: A) $-x+1, -y+1, -z+1$]

pyridine rings with centroid⋯centroid distances of 4.23 Å and 4.01 Å for **1** and **2**, respectively (Fig. 2a). Additionally, weak nonclassical C-H⋯X (X = I and Br) interactions[6] are also observed within the brick unit as listed in Table 3 (Figure S1 in Supporting Information).

The adjacent undulant 2D brick-wall layers are stacked without offset along the *a*-aixs, as shown in Figure 2b. The distance of the adjacent layers is *ca*. 8.23 Å and 8.13 Å for **1** and **2**, respectively. In crystal packing, the edge-to-face π-π interactions[7] between pyridyl groups of **L** on separated $[CuX(\mathbf{L})]_n$ bilayers are observed. (Figure S2 in Supporting Information): Dihedral angles between pyridine rings are 85.7(2)° and 87.0(3)° and distances between the centers of two pyridine ring are 5.04 Å and 4.94 Å for **1** and **2**, respectively. The crystal packing structures of both complexes are probably stabilized by C-H⋯X interactions within the layer and π-π interactions within and between the layers. The evidence for these stabilities of both complexes can be found in TG analysis. TGA traces indicate that complexes **1** and **2** in the solid states show similar thermal behaviors. They are thermally stable up to 196 °C and 205 °C for **1** and **2**, respectively, and followed by the sequent release of the ligands and the halogens (Figure S3 in Supporting Information).

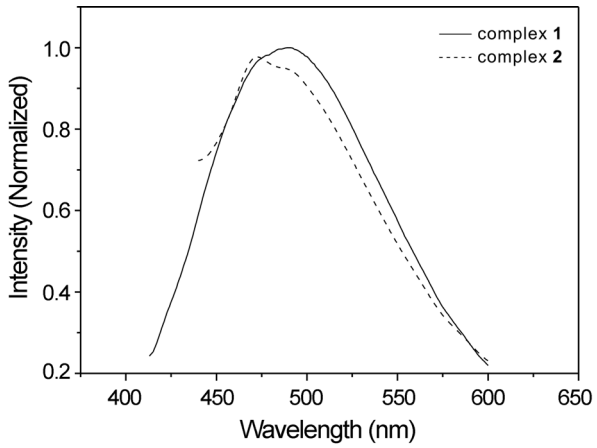


Figure 3. Solid-state emission spectra of **1** and **2** at room temperature with excitation wavelength being at 390 nm.

The photoluminescent properties of complex **1** and **2** in solid state have also been studied at room temperature. When irradiated by UV light, we observed that complex **1** and **2** showed strong blue emission (Figure S4 Supporting Information). Upon excitation at 390 nm, both complexes **1** and **2** show blue luminescence with emission maxima at 489 nm and 473 nm, respectively, as shown in Figure 3. As mentioned above, the Cu⋯Cu distances of 3.267(2) and 3.164(2) for **1** and **2**, respectively, are too long to explain cluster-centered transition caused by Cu⋯Cu interactions. Therefore, the nature of emissions for both complexes are most likely to metal-to-ligand charge transfer (MLCT) with

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

	1	**2**
Chemical formula	$C_{11}H_{11}CuIN_3$	$C_{11}H_{11}CuBrN_3$
Formula weight	375.67	328.68
T (K)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.2290(3)	8.1260(12)
b (Å)	14.2028(5)	13.971(2)
c (Å)	10.4070(4)	10.2366(16)
β (°)	107.879(1)	108.070(3)
V (Å^3)	1157.58(7)	1104.8(3)
Z	4	4
Absorption coefficient (mm^{-1})	4.527	5.565
F(000)	720	648
Crystal size (mm^3)	0.25 × 0.20 × 0.08	0.30 × 0.20 × 0.07
θ range (°)	2.51 to 27.00	2.55 to 27.00
Reflections collected/Unique	6952 / 2511	6571 / 2399
Absorption correction	Semi-empirical from equivalents (SADABS)	
Data/restraints/parameters	2511/0/146	2399/0/146
Goodness-of-fit on F^2	1.196	1.109
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0347, 0.1048	0.0687, 0.1540
(all data)	0.0389, 0.1074	0.0875, 0.1626

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** and **2**

	1	**2**
Cu1-X1	2.7074(8)	2.5495(12)
Cu1-X1^{i}	2.6514(8)	2.5134(13)
Cu1-N1	2.084(5)	2.077(6)
Cu1-N2^{ii}	2.053(5)	2.040(7)
Cu1-X1-Cu1^{i}	75.12(3)	77.36(4)
X1-Cu1-X1^{i}	104.88(3)	102.64(4)
X1-Cu1-N1	105.41(12)	105.06(16)
X1-Cu1-N2^{ii}	109.80(13)	111.97(18)
X1^{i}-Cu1-N1	115.84(13)	115.90(17)
X1^{i}-Cu1-N2^{ii}	107.20(14)	107.4(2)
N1-Cu1-N2^{ii}	113.29(19)	113.4(3)

X is either I or Br. Symmetry codes: i) $-x+1, -y+1, -z+1$; ii) $-x+1, y+0.5, -z+0.5$.

Table 3. Bond lengths (Å) and bond angles (°) of nonclassic C-H···X interactions for **1** and **2**

D-H···A	d (D-H)	d (H···A)	d (D···A)	< (DHA)
Complex **1**				
C6-H6A···I1^{i}	0.97	2.97	3.878(5)	155.7
C6-H6B···I1^{ii}	0.97	3.10	3.846(5)	134.9
C6'-H6'1···I1^{iii}	0.97	2.99	3.955(7)	171.5
Complex **2**				
C6-H6A···Br1^{i}	0.97	2.88	3.764(8)	151.2
C6-H6B···Br1^{ii}	0.97	2.99	3.753(7)	136.7
C6'-H6'1···Br1^{iii}	0.97	2.91	3.865(9)	168.6

[Symmetry codes: i) $x, -y+0.5, z-0.5$; ii) $-x+1, y-0.5, -z+0.5$; iii) $-x+1, -y+1, -z+1$].

some mixing of halide-to-metal charge transfer (XMCT) characters.[4a-c,8] It is worthy to note that examples of luminescence complexes with rhomboid Cu_2X_2 units are rare,[4] when compared to the well-known copper (I) complexes bearing cubic Cu_4X_4 units.[2]

In summery, two Cu(I)-halide complexes with the formula $[CuX(\mathbf{L})]_n$ (X = I (**1**) and Br (**2**), **L** = dipyridyl ligand) were prepared and characterized fully their structures. Both complexes are isostructures and 2D brick-wall type coordination polymers, in which rhomboid Cu_2I_2 nodes interconnect dipyridyl ligands **L**. The investigation on photophysical properties of **1** and **2** shows that the nature of emission can be attributed to the metal-to-ligand charge transfer with the contribution of halide-to-metal charge transfer. This is the unique photophysical property in that the example of copper(I) complex having rhomboid Cu_2X_2 unit is very scarce.

Experimental Section

All commercial reagents including solvents were of analytical reagent grade where available. NMR spectra were recorded on a Bruker DRX-300 spectrometer (300 MHz). The IR spectra were recored on a VERTEX 80v FT-IR spectrometer with KBr pellet in the range 4000-400 cm^{-1}. Elemental analysis was carried out on a CHNS-932 elemental analyzer. Thermogravimetric analysis (TGA) was performed under nitrogen on a SDT Q600 thermogravimetric analyzer. The sample was heated using a 10 °C/min heating rate from 25 to 900 °C. The solid-state excitation and emission spectra were performed on a RF-5301 spectrophotometer.

Preparation of *N,N*-(2-pyridyl)(2-pyridylmethyl)amine (L). L was synthesized according to literature procedure.[9]

Preparation of $[CuI(L)]_n$ (1): A solution of MeCN (5 mL) containing CuI (19.0 mg, 0.1 mmol) was introduced into a glass tube and layered with MeCN as a buffer zone. Then a MeCN solution (5 mL) of **L** (18.5 mg, 0.1 mmol) was added carefully to avoid possible mixing. After standing at room temperature for 1 day, reddish brown crystals suitable for X-ray analysis were obtained at the wall of glass tube. The crystals were filtered and washed with acetonitrile and diethyl ether (yield 76%). IR (KBr, ν, cm^{-1}) 3339 (m, N-H), 3292 (m, C-H, aromatic), 1608 (s, C=N, py), 1569 (s, C=C, py). $[CuI(\mathbf{L})]_n$ Anal. Calcd for $C_{11}H_{11}N_3CuI$: C, 35.17, H, 2.95, N, 11.19. Found: C, 35.43, H, 2.78, N, 10.96%.

Preparation of $[CuBr(L)]_n$ (2): This compound was prepared in the same way as for **1** using CuBr (14.3 mg, 0.1 mmol) instead of CuI (yield 68%). IR (KBr, ν, cm^{-1}) 3338 (m, N-H), 3292 (m, C-H, aromatic), 1608 (s, C=N, py), 1571 (s, C=C, py). $[CuBr(\mathbf{L})]_n$ Anal. Calcd for $C_{11}H_{11}N_3CuBr$: C, 40.20, H, 3.37, N, 12.78. Found: C, 40.49, H, 3.28, N, 12.56%.

X-ray crystallography: Single crystal diffraction data of **1** and **2** were collected on a Bruker Smart diffractometer equipped with a graphitemonochromated Mo $K\alpha$ (λ = 0.71073 Å) radiation source and a CCD detector. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 5 sec. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT-plus.[10] Empirical absorption corrections were applied to the data sets using the SADABS.[11] The structure was solved by direct methods and refined by full matrix least squares methods on F^2 for all data using SHELXTL software.[12] Judging from the difference in the displacement parameters, discrimination was impossible for carbon and nitrogen atoms of -CH_2-NH- fragments of **L** in complexes **1** and **2**. Therefore, the locations of the C or N atoms were modeled with each position of -CH_2-NH- fragment assigned occupancy of 50% C and 50% N, and the thermal parameters of C and N on the same site constrained to be equal. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom. Crystallographic data and structural refinement data for **1** is summarized in Table 1.

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Supplementary material. Supplementary crystallographic data associated to complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 689430 and 689431, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), or electronically *via www.ccdc.cam.ac.uk/perl/catreq.cgi*. Supplementary figures, TGA, and photoluminescence photos of both complexes are available *via* the internet at *http://www.kcsnet.or.kr/bkcs*.

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