Self-Assembled Copper(I) Complexes of Symmetric Dithioether Ligands

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Coordination polymer is being investigated very actively due to many interesting structural features and useful properties such as catalysis, photoluminescence, magnetism, and adsorption.[1-4] Copper(I) halides are capable of adopting various structural motifs.[5-8] Recently, we have focused on Cu(I) coordination polymers with dithioether ligands. During our investigation on CuI reaction with dithioether ligands, we examined the structural diversity of copper(I) iodide complexes by symmetric and asymmetric dithioether ligands.[6a,9,10] Herein, we report a discrete complex (**1**), two-(**2**), and one-dimensional (**3**) coordination polymers based on 1,2- (**L^1**), 1,3- (**L^2**), and 1,4-bis(cyclohexylthiomethyl)-benzene (**L^3**), respectively (Scheme 1).

Three bidentate dithioether ligands **L^1**-**L^3** were synthesized by the reaction of cyclohexanethiol and each corresponding bis(bromomethyl)benzene. An equimolar amount of copper(I) iodide and **L^1** was dissolved in acetonitrile. Vapor diffusion of diethyl ether into acetonitrile solution of the reactants resulted in a colorless X-ray quality crystal **1**. Single-crystal X-ray analysis[11] revealed that **1** was a formula [Cu$_2$I$_2$**L^1**$_2$] and its gross geometry of **1** can be described as a sandwich type complex (Figure 1). The asymmetric unit

consists of one **L^1** and one copper(I) iodide. A sandwich unit of **1** contains two asymmetric units where two ligands are bridged by rhomboid Cu-I$_2$-Cu linkers. The copper(I) is tetrahedrally coordinated by two sulfur donors from each ligand and two μ_2-iodide atoms. The S-Cu and Cu-I bond distances are reasonably similar to those reported in other complexes.[5,6]

Slow evaporation of acetonitrile solution of **L^2** with an equivalent amount of copper(I) iodide afforded a yellow crystal **2** that was suitable for an X-ray analysis (Figure 2).[11] Polymer **2** can be described as a 2-dimensional (2D) infinite brick-wall type complex with formula [CuI**L^2**]$_n$. The asymmetric unit consists of one **L^2** and one copper(I) iodide. A single brick unit of **2** contains four asymmetric units where each ligand is interconnected with the rhomboid Cu-I$_2$-Cu linkers alternately (Figure 2b). The copper(I) is tetrahedrally coordinated by two sulfur donors from two adjacent ligands and two μ_2-iodide atoms. In this case, the preference of 2D sheet is probably due, at least in part, to the planarity of four sulfur donors (S1, S1B, S2A and S2C) related by an inversion symmetry, which also applies to that of **1**. However, the fact that **L^1** has not only shorter distance between
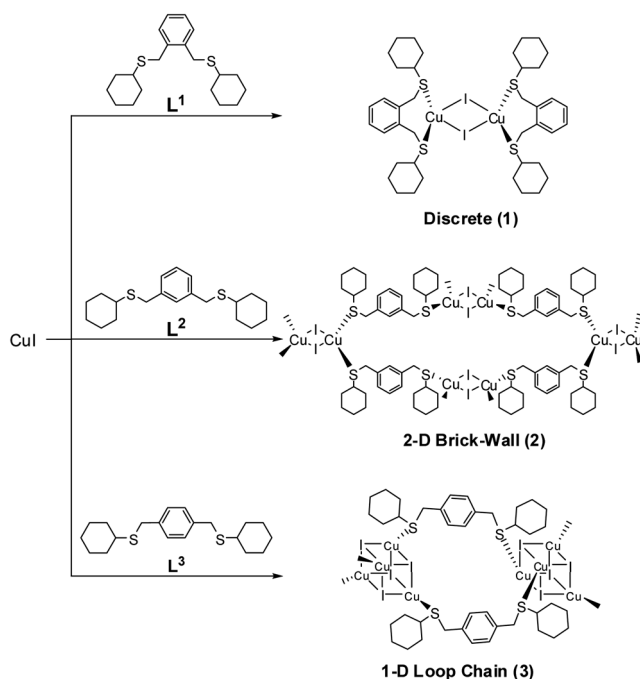
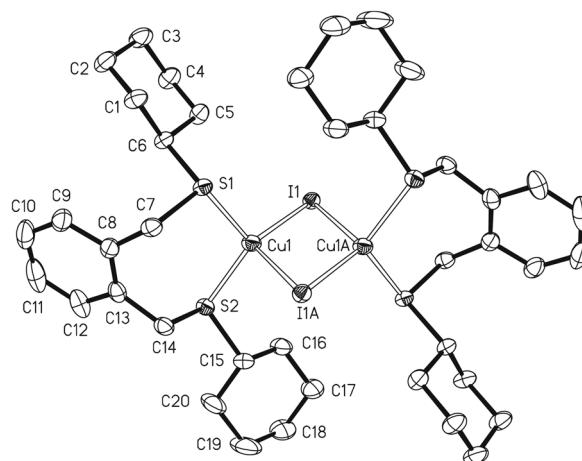**Scheme 1**. Syntheses of Cu(I) complexes **1-3**.

Figure 1. Ortep diagram of **1**, showing coordination environment. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-Cu1A 2.9560(5), S1-S2 3.8797(6), Cu1-S2 2.3188(5), Cu1-S1 2.3200(5), Cu1-I1 2.5804(3), Cu1-I1A 2.7285(3), S1-(center of the phenylene ring)-S2 58.62, S2-Cu1-S1 113.513(18), S2-Cu1-I1 115.823(15), S1-Cu1-I1 115.218(14), S2-Cu1-I1A 102.216(14), S1-Cu1-I1A 94.839(14), I1-Cu1-I1A 112.394(9), Cu1-I1-Cu1A 67.606(9). [Symmetry codes: A = −x + 1, −y + 1, −z + 1]

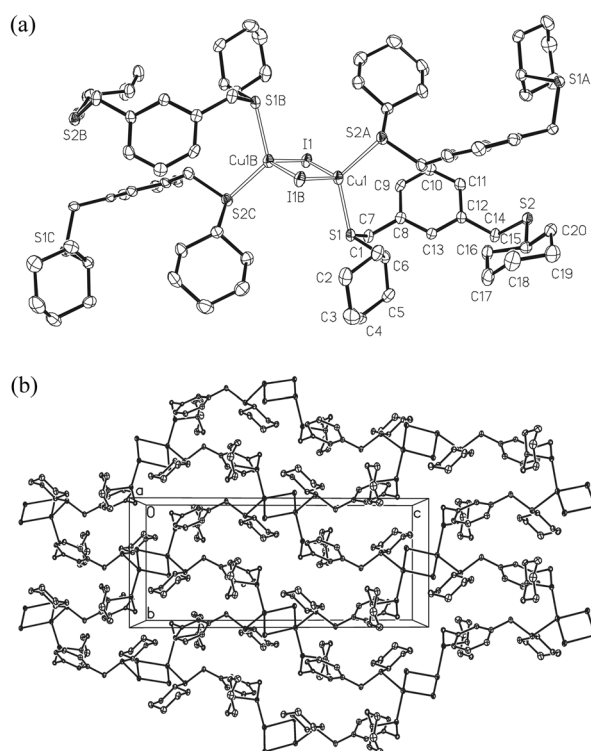500 *Bull. Korean Chem. Soc.* **2008**, Vol. 29, No. 2

Notes

(a)

(b)

Figure 2. (a) Ortep diagram of **2**, showing coordination environment and (b) perspective view along the *a*-axis. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu1-Cu1B 2.7566(9), S1-S2 6.9171(13),Cu1-S2A 2.3400(10), Cu1-S1 2.3523(11), Cu1-I1 2.6224(5), Cu1-I1B 2.6841(5), S1-(center of phenylene ring)-S2 116.63, S2A-Cu1-S1 122.11(4), S2A-Cu1-I1 113.50(3), S1-Cu1-I1 100.51(3), S2A-Cu1-I1B 98.84(3), S1-Cu1-I1B 105.26(3), I1-Cu1-I1B 117.420(17), Cu1-I1-Cu1B 62.581(17). [Symmetry codes: A = −x + 3/2, y + 1/2, −z + 1/2; B = −x + 2, −y + 2, −z + 1; C = −x + 3/2, y − 1/2, −z + 1/2]

S1 and S2 but also smaller angle (S1-center of xylene-S2) than those of **L²** leads to the formation of the sandwich type complex. The adjacent 2D brick-wall layer is stacked on the top of this layer without offset in the *bc*-plane such that the continuous channels among the *a*-axis are formed. The distance of the adjacent layers is *ca.* 10.4 Å, indicating no significant close contacts or other interactions between layers in the packing.

For complex **3**, Cu_4I_4 units are located at the nodes of loop chain frameworks (Figure 3). Each copper atom in the cubane-type Cu_4I_4 unit is tetrahedrally coordinated to three μ_3-iodide atoms and one sulfur donor of **L³**. Accordingly, four Cu-S bonds between the cubane core and sulfur donors coming from four different **L³** ligands occupy well-separated positions, and these adjacent ligand molecules are arranged spaciously to minimize steric hindrance. The cubane cores were interconnected with the ligands through Cu-S bonds to produce (2+2)-type large metallacycles, leading to the formation of a 1D loop chain structure.

Upon irradiation by UV light (λ_{ex} = 323 nm), only **3** which has CuI cubane cores exhibits a bright green emission (λ_{max} = 521 nm) in the solid state due to cluster-centered excited state by mixed halide-to-metal charge transfer character
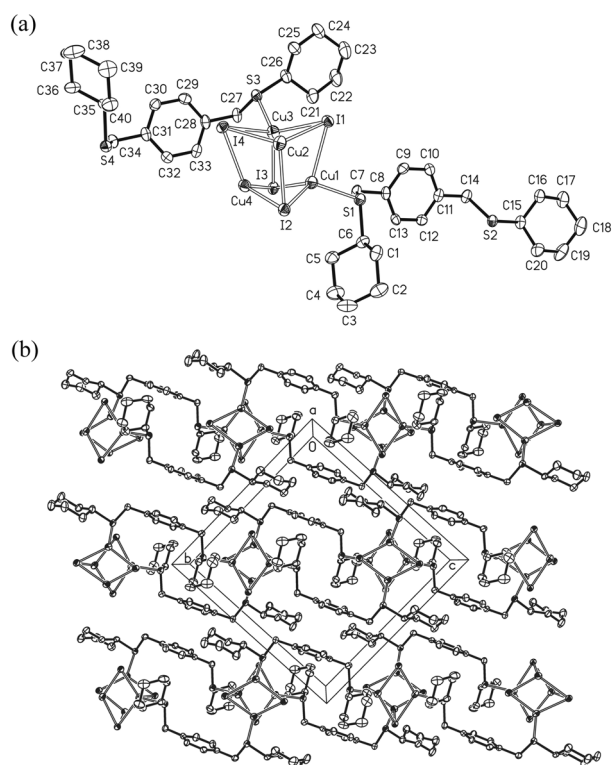
(a)

(b)

Figure 3. (a) Ortep diagram of **3**, showing a cubane-like Cu_4I_4 core and (b) perspective view along the *a*-axis. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Cu(1)-Cu(2), 2.8568(8), Cu(1)-Cu(3), 2.8250(8), Cu(1)-Cu(4), 2.7719(8), Cu(2)-Cu(3), 2.7899(8), Cu(2)-Cu(4), 2.8046(8), Cu(3)-Cu(4), 2.8303(8), Cu1-S1 2.3162(12), Cu2-S2A 2.3191(13), Cu3-S3 2.3161(13), Cu4-S4B 2.3163(12), S1-(center of phenylene ring)-S2 130.15, S1-(center of phenylene ring)-S2 129.29, S1-Cu1-I3 106.45(4), I2-Cu1-I1 115.77(2), S2A-Cu2-I1 101.73(3), S3-Cu3-I1 116.21(4), S4B-Cu4-I3 119.53(4). [Symmetry codes: A = −x + 1, −y + 1, −z + 1; B = −x + 1, −y + 2, −z]

(Figure 4).[6a,12] The emission wave length is shorter than that of similar cubane cluster in the literature.[6a] This can be explained by higher energy level of LUMO with bonding character[12] owing to longer Cu-Cu distances (2.7719-2.8568 Å) than those (2.7290-2.7547 Å)[13] of the similar cubane cluster at 173 K.

In summary, the present study represents that the entirely different coordination compounds **1**-**3** are induced by a structural difference in the ligands **L¹**-**L³** with the identical formula. The origin of the three different coordination compounds is due to the structural difference in the ligands **L¹**-**L³**, which have all different angles and distances between the two sulfur donors. In the case of **1**, the shortest distance and angle between the two sulfurs and the copper give rise to the formation of the sandwich type structure. However, longer S···S distance than **L¹** and the planarity of four sulfur donors bound to the planar rhomboid Cu-I_2-Cu unit in **2** prefer 2D layer structure. The 1D loop chain structure (**3**) is formed by the longest S···S distance and the spacious cubane-type Cu_4I_4 unit that allow connection between different Cu_4I_4 units and the packing of bulky cyclohexyl groups.

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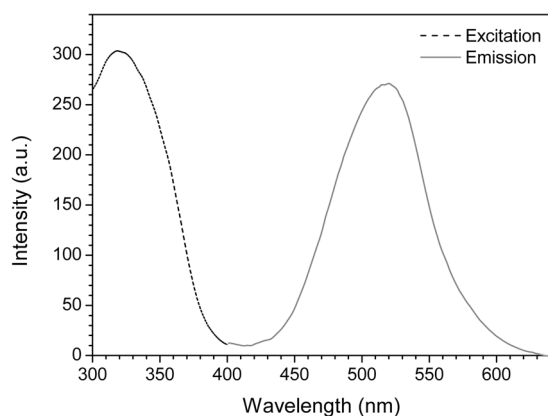**Figure 4**. Solid state excitation (dashed line) and emission (solid line) spectra of **3**.

Experimental Section

The ^1H and ^{13}C NMR spectra were recorded with a Bruker Advance-300 (300 MHz) NMR spectrometer. Mass spectra were obtained on a JEOL JMS-700 spectrometer. The FT-IR spectra of the coordination polymers were measured with a Shimadzu FT-IR 8100 spectrometer. The elemental analysis was carried out on a LECO CHNS-932 elemental analyzer. Solid state luminescence spectra were acquired with a Perkin Elmer LS 50B spectrophotometer at the Central Laboratory of Gyeongsang National University. The excitation and emission spectra were corrected for the wavelength-dependent lamp intensity and detector response, respectively. The pulsed excitation source was generated using the 323 nm of the Xenon lamp. Single crystal diffraction data for **1-3** at 173 K were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 45 collected frames) using the SMART program. The intensity data were processed using the Saint Plus program. All of the calculations for the structure determination were carried out using the SHELXTL package (version 5.1).[14] In most cases, hydrogen positions were input and refined in a riding manner along with the attached carbons.

1,2-Bis(cyclohexylthiomethyl)benzene (L^1). NaOH (0.80 g, 0.02 mol) was dissolved in water (30 mL) and cyclohexanethiol (2.32 g, 0.02 mol) dissolved in THF (20 mL) was added and stirred. 1,2-bis(bromomethyl)benzene (1.75 g, 0.01 mol) was dissolved in THF (20 mL) and added to the cyclohexanethiol solution. After reflux for 2 h, the reaction mixture was cooled and acidified by adding 6 M HCl. Organic layer was collected and water layer was extracted with THF. The combined organic layers dried with anhydrous sodium sulfate were evaporated to give crude oil. Column chromatography (silica gel, *n*-hexane/ethylacetate = 50/50 (v/v), R$_f$ 0.4) gave pure oil (3.08 g, 90%). IR (KBr, ν, cm^{-1}): 3061 w, 3018 w, 2926 s, 2853 s, 2660 w, 1697 w, 1600 w, 1489 m, 1448 s, 1339 m, 1263 m, 1200 m, 997 m, 885 m, 766 m, 716 m, 599 w, 563 w. ^1H NMR (300 MHz,

CDCl$_3$): δ 7.25 (m, 4H Ar), 3.94 (s, 4H CH$_2$ArCH$_2$), 2.67 (m, 2H SCH), 1.2-2.1 (m, 20H, CH$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.78, 130.38, 127.17, 43.79, 33.52, 31.93, 26.05, 25.86. HREI-MS (*m/z*) calcd. for C$_{20}$H$_{30}$ S$_2$ [M]$^+$: 334.1789; found: 334.1790.

1,3-Bis(cyclohexylthiomethyl)benzene (L^2). This compound was prepared in a manner analogous to that for **L^1**. Column chromatography (silica gel, *n*-hexane/ethylacetate = 50/50 (v/v), R$_f$ 0.5) gave pure oil (3.00 g, 87%). IR (KBr, ν, cm^{-1}): 3055 w, 3024 w, 2926 s, 2850 s, 2665 w, 1697 w, 1604 w, 1487 w, 1448 s, 1340 w, 1263 m, 1202 m, 999 m, 887 w, 796 w, 710 m, 446 w. ^1H NMR (300 MHz, CDCl$_3$): δ 7.25 (m, 4H Ar), 3.74 (s, 4H CH$_2$ArCH$_2$), 2.56 (m, 2H SCH), 1.2-2.1 (m, 20H, CH$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 139.14, 129.16, 128.53, 127.24, 42.94, 34.51, 33.39, 25.99, 25.86. HREI-MS (*m/z*) calcd. for C$_{20}$H$_{30}$ S$_2$ [M]$^+$: 334.1789; found: 334.1789.

1,4-Bis(cyclohexylthiomethyl)benzene (L^3). This compound was prepared in a manner analogous to that for **L^1**. Column chromatography (silica gel, *n*-hexane/ethylacetate = 50/50 (v/v), R$_f$ 0.4) gave pure solid (2.73 g, 82%). m.p. 67.5 ^{o}C, IR (KBr, ν, cm^{-1}): 3046 w, 3025 w, 2928 s, 2850 s, 2652 w, 1692 w, 1510 m, 1450 s, 1341 w, 1262 m, 1195 m, 998 m, 887 m, 845 m, 744 m, 718 m, 511 m. ^1H NMR (300 MHz, CDCl$_3$): δ 7.27 (m, 4H Ar), 3.75 (s, 4H CH$_2$ArCH$_2$), 2.55 (m, 2H SCH), 1.2-2.1 (m, 20H, CH$_2$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 137.44, 128.86, 42.96, 34.32, 33.41, 26.01, 25.88. HREI-MS (*m/z*) calcd. for C$_{20}$H$_{30}$ S$_2$ [M]$^+$: 334.1789; found: 334.1791.

[Cu$_2$I$_2$L^1$_2$] (1): An acetonitrile solution (5 mL) of **L^1** (0.040 g, 0.10 mmol) was allowed to mix with an acetonitrile solution (5 mL) of CuI (0.019 g, 0.10 mmol), followed by diethyl ether diffusion. Colorless single crystals suitable for X-ray analysis were obtained. The crystals were filtered and washed with diethyl ether/acetonitrile (v/v = 1/1) solution (0.048 g, 82%). m.p. 182-184 ^{o}C, IR (KBr, ν, cm^{-1}): 2923 s, 2848 m, 1493 w, 1447 m, 1333 w, 1262 w, 1205 w, 996 w, 882 w, 769 w, 740 w, 703 w, 669 w. [Cu$_2$I$_2$L^1$_2$] Anal. Calcd for C$_{40}$H$_{60}$S$_4$Cu$_2$I$_2$: C, 45.75, H, 5.76, S 12.21. Found: C, 45.67, H, 5.98, N, 3.23, S 11.98%.

[CuIL^2]$_n$ (2): This compound was prepared in a manner analogous to that for **1**. (0.050 g, 85%). m.p. 182-185 ^{o}C, IR (KBr, ν, cm^{-1}): 2928 s, 2846 m, 1597 w, 1484 w, 1442 m, 1346 w, 1264 w, 1222 w, 1160 w, 1084 w, 995 w, 905 w, 850 w, 806 w, 711 m, 601 w, 568 m, 443 m. [CuIL^2]$_n$ Anal. Calcd for C$_{20}$H$_{30}$S$_2$CuI: C, 45.75, H, 5.76, S 12.21. Found: C, 45.79, H, 5.86, S 11.86%.

[Cu$_4$I$_4$L^3$_2$]$_n$ (3): This compound was prepared in a manner analogous to that for **1** except for an amount of CuI (0.038 g, 0.20 mmol). (0.054 g, 69%). m.p. 193-195 ^{o}C, IR (KBr, ν, cm^{-1}): 2923 s, 2846 m, 1640 s, 1425 s, 1286 m, 1200 s, 1025 m, 985 m, 891 m, 557 w, 527 w, 496 w. [Cu$_4$I$_4$(**L^3**)$_2$]$_n$ Anal. Calcd for C$_{40}$H$_{60}$S$_4$Cu$_4$I$_4$: C, 33.57, H, 4.23, S 8.96. Found: C, 33.81, H, 4.35, S 9.25%.

Supplementary material. Supplementary crystallographic data associated with **1-3** have been deposited at the Cam-

bridge Crystallographic Data Centre [CCDC deposit numbers 649208 (**1**), 649209 (**2**), and 649210 (**3**)]. These data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically *via* www.ccdc.ac.uk/data_request/cif.

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11. Crystallographic data for $C_{40}H_{60}Cu_2I_2S_4$ (**1**): FW = 1050.00, monoclinic, space group $P2_1/c$ (no. 14), a = 10.9341(5), b = 8.8896(4), c = 22.1228(10) Å, β = 97.2980(10)^o, V = 2132.91(17) Å^3, Z = 2, D_c = 1.635 g cm^{-3}, T = 173(2) K, $F(000)$ = 1056 variables refined with 5000 independent reflections (R_{int} = 0.0162) to final R indices [$I > 2\sigma(I)$] of R_1 = 0.0191 and wR_2 = 0.0458, and GOF = 1.043, absorption correction: SADABS (T_{min}/T_{max} = 0.761239).
    Crystallographic data for $C_{20}H_{30}CuIS_2$ (**2**): FW = 525.00, monoclinic, space group $P2_1/n$ (no. 14), a = 11.8523(9), b = 8.6406(7), c = 20.0139(16) Å, β = 92.853(2)^o, V = 2047.1(3) Å^3, Z = 4, D_c = 1.703 g cm^{-3}, T = 173(2) K, $F(000)$ = 1056 variables refined with 4787 independent reflections (R_{int} = 0.0708) to final R indices [$I > 2\sigma(I)$] of R_1 = 0.0330 and wR_2 = 0.0584, and GOF = 0.882, absorption correction: ψ-scan (T_{min} = 0.1557, T_{max} = 0.3297).
    Crystallographic data for $C_{40}H_{60}Cu_4I_4S_4$ (**3**): FW = 1430.88, triclinic, space group P-1 (no. 2), a = 11.2171(5), b = 14.3433(7), c = 14.8236(7) Å, α = 92.2170(10), β = 90.4880(10), γ = 93.7800(10)^o, V = 2377.86(19) Å^3, Z = 2, D_c = 1.998 g cm^{-3}, T = 173(2) K, $F(000)$ = 1384 variables refined with 10865 independent reflections (R_{int} = 0.0504) to final R indices [$I > 2\sigma(I)$] of R_1 = 0.0321 and wR_2 = 0.0628, and GOF = 1.008, absorption correction: ψ-scan (T_{min} = 0.1967, T_{max} = 0.3080).
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