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Hard/Soft Heterometallic Network Complex of a Macrocycle with Endo/Exocyclic Coordination

Yongnu Jin,[†] Hyun Jee Kim,[†] Jai Young Lee,[†,‡] So Young Lee,[†] Won Joon Shim,[§] Sang Hee Hong,[§] and Shim Sung Lee*,[†]

[†]Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, South Korea, [‡]Department of Chemistry, Konyang University, Nonsan 320-711, South Korea, and [§]Oil & POP Research Group, Korea Ocean Research and Development Institute, 391 Jangmok-myon, Geoje 656-830, South Korea

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One-pot assembly reactions of an S_2O_4 macrocycle with CuI in the absence and presence of KI afforded an emissive one-dimensional looped coordination polymer linked with a cubane-type copper iodide cluster and an endocoordinated potassium(I) coordination polymer linked with a ribbon-type copper iodide cluster, respectively.

Related to the existence of a central cavity, macrocyclic ligands have long been employed to tune such ring systems for endocyclic metal-ion recognition.[1] Thiamacrocycles, however, often form not only endocyclic (*metal-in-cavity*) complexes but also exocyclic ones in which the metal ions exist also outside the cavity.[2] Indeed, a range of mono- and multinuclear complexes of thiamacrocycles with exocoordination have been reported by us[3] and others.[4] We recently suggested that such endo- and exocoordination could be controlled by using the discriminating anion coordination ability.[5] Such an anion effect on the metal position was successfully employed to illustrate how the coordinating ability of the anion controls a color change through the formation of endo- and exocyclic complexes with an *N*-azo-coupled NO_2S_2 macrocycle system.[6]

On the other hand, the self-assembly process involving copper(I) halides and multinuclear ligands often leads to discrete complexes and continuous ones because the copper(I) halides are capable of adopting a variety of structural motifs such as rhomboid dimers, cubanes, hexagonal prisms, one-dimensional (1D) chains, and double-stranded stairs.[7] Further, numerous copper(I) halide complexes ranging from mononuclear species to long-chain polymers are luminescent.[8] We recently reported calix[4]bis(dithiacrown)-based, endocoordinated disilver(I) complexes as well as an exocoordianted three-dimensional (3D) network connected by CuI-based clusters.[3h] Also, we have reported 3D CuI coordination networks of calix[4]bis(dithiacrown) that show crystal-to-crystal transformation on coordinated solvent removal accompanying irreversible[3e] and reversible[3f] solvatophotoluminescences.

Not only are we interested in investigating the factors that influence the self-assembly of metal complexes into distinct endo- or exocoordinated products, but we also want to advance our understanding of a methodology of emerging significance in macrocyclic chemistry that may serve as a potent controllable phenomenon.

As part of ongoing efforts, we have focused our attention on a hard/soft heteronuclear macrocyclic complex system that would potentially influence the coordinated metal-ion position as well as networking. In the present study, KI and CuI have been employed to investigate how the resulting

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*To whom correspondence should be addressed. E-mail: sslee@gnu.ac.kr.

(1) (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1991**, *91*, 1721. (b) Lindoy, L. F. *Coord. Chem. Rev.* **1998**, *174*, 327. (c) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S. *Chem. Rev.* **1995**, *95*, 2529.

(2) (a) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (b) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328. (c) Hill, S. E.; Feller, D. *J. Phys. Chem. A* **2000**, *104*, 652.

(3) (a) Kim, H. J.; Sultana, K. F.; Lee, J. Y.; Lee, S. S. *CrystEngComm* **2010**, *12*, 1494. (b) Lee, J. Y.; Kim, H. J.; Park, C. S.; Sim, W.; Lee, S. S. *Chem.—Eur. J.* **2009**, *15*, 8989. (c) Lee, J. Y.; Lee, S. Y.; Park, S.; Kwon, J.; Sim, W.; Lee, S. S. *Inorg. Chem.* **2009**, *48*, 8934. (d) Park, S.; Lee, S. Y.; Lee, S. S. *Inorg. Chem.* **2010**, *49*, 1238. (e) Lee, J. Y.; Lee, S. Y.; Sim, W.; Kim, J.; Lee, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 6902. (f) Lee, J. Y.; Kim, H. J.; Jung, J. H.; Sim, W.; Lee, S. S. *J. Am. Chem. Soc.* **2008**, *130*, 13838. (g) Lee, S. Y.; Park, S.; Kim, H. J.; Jung, J. H.; Lee, S. S. *Inorg. Chem.* **2008**, *47*, 1913. (h) Lee, J. Y.; Lee, S. Y.; Seo, J.; Park, C. S.; Go, J. N.; Sim, W.; Lee, S. S. *Inorg. Chem.* **2007**, *46*, 6221. (i) Yoon, I.; Seo, J.; Lee, J.-E.; Park, K.-M.; Lah, M. S.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 3487.

(4) (a) Robinson, G. H.; Sangokova, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494. (b) Buter, J.; Kellog, R. M.; van Bolhuis, F. *J. Chem. Soc., Chem. Commun.* **1991**, 910. (c) Blake, A. J.; Gould, R. O.; Parsons, S.; Radek, C.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2374. (d) Heller, M.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1191. (e) de Groot, B.; Jenkins, H. A.; Loeb, S. J. *Inorg. Chem.* **1992**, *31*, 203. (f) Grant, G. J.; Galas, D. F.; Jones, M. W.; Loveday, K. D.; Pennington, W. T.; Schimek, G. L.; Eagle, C. T.; Van Derveer, D. G. *Inorg. Chem.* **1998**, *37*, 5299.

(5) Kim, H. J.; Lee, S. S. *Inorg. Chem.* **2008**, *47*, 10807.

(6) (a) Lee, S. J.; Jung, J. H.; Seo, J.; Yoon, I.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Org. Lett.* **2006**, *8*, 1641. (b) Lee, H.; Lee, S. S. *Org. Lett.* **2009**, *11*, 1393.

(7) Graham, P. M.; Pike, R. D.; Sabat, M.; Bailey, R. D.; Pennington, W. T. *Inorg. Chem.* **2000**, *39*, 5121.

(8) (a) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267. (b) Babich, O. A.; Kokozay, V. N. *Polyhedron* **1997**, *16*, 1487. (c) Ashton, P. R.; Burns, A. L.; Claessens, C. G.; Shimizu, G. K. H.; Small, K.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1493. (d) Vitale, M.; Palke, W. E.; Ford, P. C. *J. Phys. Chem.* **1992**, *96*, 8329. (e) Kim, T. H.; Lee, K. Y.; Shin, Y. W.; Moon, S.-T.; Park, K.-M.; Kim, J. S.; Kang, Y.; Lee, S. S.; Kim, J. *Inorg. Chem. Commun.* **2005**, *8*, 27.

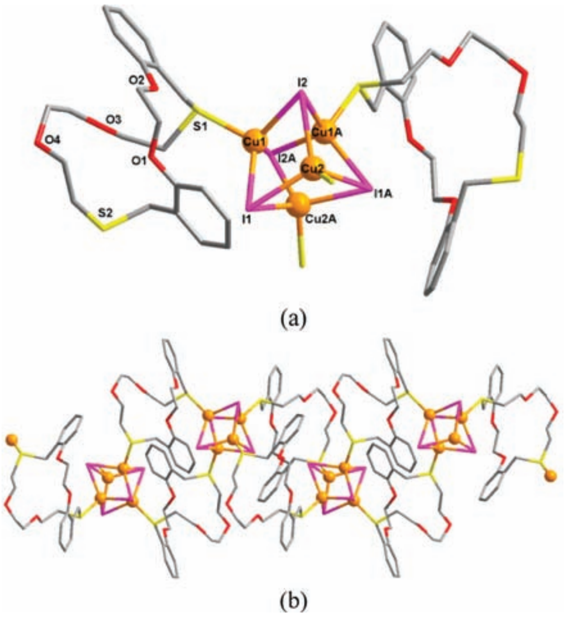
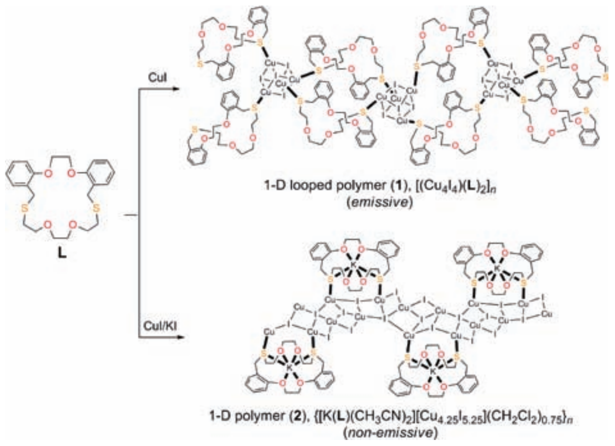


Figure 1. (a) Coordination environment of exocyclic copper(I) iodide complex **1**, $[(\mu_4\text{-}Cu_4I_4)(\mathbf{L})_2]_n$, and (b) its 1D looped-chain network structure linked with a cubane-type Cu_4I_4 cluster.

Scheme 1. 1D Network Complexes of **L** Prepared in This Work



products are influenced by the use of either metal. The proposed dibenzo-type O_4S_2 macrocycle **L**[9] (Scheme 1) employs two S donors as bridgeheads for the required exocoordination, which, in turn, serves to minimize the softness of the crown ring. This approach enabled us to prepare two distinct 1D coordination polymers **1** and **2** from one-pot reactions of **L** with CuI in the absence and presence of KI, respectively, as depicted in Scheme 1. Herein we report their synthesis and crystal structures along with the photoluminescent properties.

L was prepared according to our previously published method.[9] Liquid−liquid diffusion of CuI in acetonitrile onto a dichloromethane solution of **L** upon standing afforded the colorless crystalline product **1**. Single-crystal X-ray analysis revealed that **1** is a 1D polymeric array of formula $[(Cu_4I_4)(\mathbf{L})_2]_n$ (Figure 1). The asymmetric unit of the complex part of **1** contains one **L**, two Cu atoms, and two I atoms. The cubane-type Cu_4I_4 cluster cores are located at the center of four **L**, and each cluster core is tetrahedrally coordinated by four S donors from four adjacent **L** by Cu−S bonds [2.300(1) and 2.316(1) Å], forming an infinite 1D poly(cyclic dimer) structure. The Cu_4I_4 moiety defines a slightly irregular cubane-type arrangement of alternating Cu and I atoms.[10] Two crystallographically independent Cu centers have similar geometry. Each Cu atom is in a distorted tetrahedral coordination environment, being linked to three μ_3-I atoms and one S donor of **L**. Accordingly, four Cu−S bonds [2.300(1)−2.316(1) Å] between the cubane core and S donors coming from four adjacent ligands occupy well-separated positions, and these ligand molecules are arranged spaciously to minimize steric hindrance.

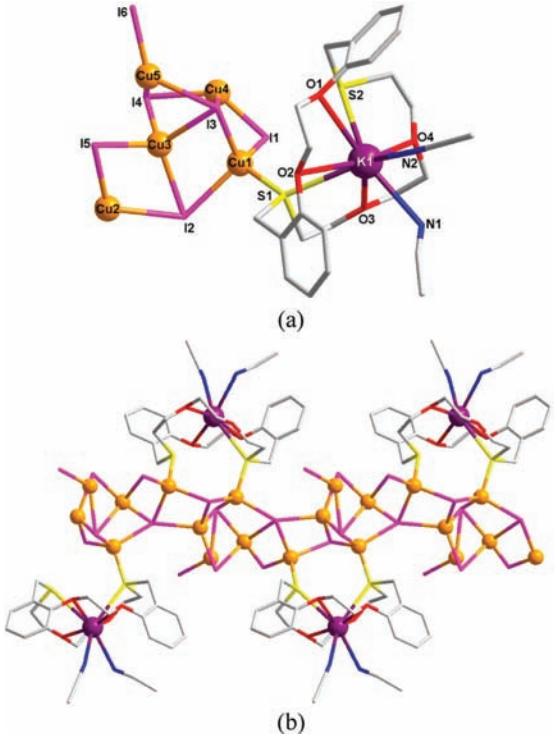


Figure 2. (a) Coordination environment of endocyclic potassium(I) and exocyclic copper(I) iodide heteronuclear complex **2**, $\{[K(\mathbf{L})(CH_3CN)_2][Cu_{4.25}I_{5.25}](CH_2Cl_2)_{0.75}\}_n$ and (b) its 1D network structure linked with a ribbon-type copper(I) iodide cluster. The noncoordinating solvent molecule was omitted.

Having obtained the copper(I) iodide network complex of **L**, we then proceeded to the preparation of the corresponding heteronuclear complex by employing **1** as a precursor. However, **1** is almost insoluble in most common solvents and only sparingly soluble in warm dimethyl sulfoxide, where a subsequent decomposition is observed. So further reactions using **1** was not available. When the metal salt was changed from CuI to CuI plus KI in an one-pot assembly reaction with **L**, the colorless crystalline product **2** was successfully obtained. X-ray analysis revealed that **2** is a 1D network of formula $\{[K(\mathbf{L})(CH_3CN)_2][Cu_{4.25}I_{5.25}](CH_2Cl_2)_{0.75}\}_n$ involving a heteronuclear K^I/Cu^I unit, in which two different metals positioned inside and outside the cavity (Figure 2). Interestingly, the array structure of **2** resembles the shape of the ribbon with some pendent: a copper(I) iodide cluster backbone as the ribbon and

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[9] Lee, Y. H.; Lee, S. S. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *39*, 235.

[10] (a) Kim, T. H.; Park, G.; Shin, Y. W.; Park, K.-M.; Choi, M. Y.; Kim, J. *Bull. Korean Chem. Soc.* **2008**, *29*, 499. (b) Cariati, E.; Bu, X.; Ford, P. C. *Chem. Mater.* **2000**, *12*, 3385. (c) Kim, T. H.; Shin, Y. W.; Jung, J. H.; Kim, J. S.; Kim, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 685. (d) Leung, W.-P.; So, C.-W.; Chong, K.-H.; Kan, K.-W.; Chan, H.-S.; Mak, T. C. W. *Organometallics* **2006**, *25*, 2851. (e) Churchill, M. R.; Kaira, K. L. *Inorg. Chem.* **1974**, *13*, 1899.

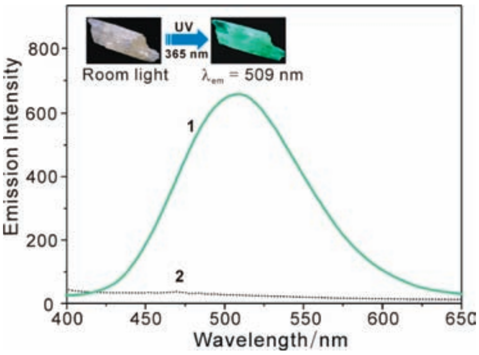

Figure 3. Solid-state photoluminescence spectra of **1** and **2** at room temperature (excitation at 365 nm).

the macrocyclic potassium(I) complex unit as the pendent. The K^I ion in the cavity is eight-coordinated, with coordination to four O and two S atoms from **L**. The remaining two sites are occupied by two acetonitrile solvent molecules from the opposite side of the copper(I) iodide ribbon. The bond angles around the K atom vary from 54.6(2) to 167.6(2)°. The K−O [2.763(6)−3.082(6) Å] and K−S [3.176(2) and 3.301(3) Å] bond distances are slightly longer than those reported previously for such bonds.[11] This could be a result of the high coordination number of the K atom in this complex. Unlike the case of **1**, **2** possesses four crystallographically independent Cu atoms linked by two I atoms, forming a rhomboidal $Cu-I_2-Cu$ unit in a ribbon structure. The local coordination environment of four Cu atoms shows two different modes. The Cu1 and Cu3 atoms are in a distorted tetrahedral coordination environment, being coordinated to three μ_3-I atoms and one S donor of **L**. The Cu2 and Cu4 atoms are also in a tetrahedral coordination environment with four coordination sites occupied by four I atoms. Consequently, potassium(I) iodide induced not only the endocyclic complexation of the K^I ion but also the rearrangement of the copper(I) iodide cluster by coordination of an I ion.

Because the photoluminescence behavior of copper(I) halide cluster based thiamacrocyclic complexes is often very dependent on their structures,[3f] the luminescent properties of the present systems were compared. The photoluminescent properties of the above products were investigated in the solid state at room temperature. Compound **2** displays no photoluminescence in the solid state, while **1** exhibits strong blue-green emission with the maximum intensity at 509 nm (λ_{ex} = 365 nm; Figure 3). A similar emission band from 489 to 568 nm was also observed previously for other cubane-type copper(I) halide clusters because of the cluster-centered excited state with mixed halide-to-metal charge-transfer character.[10]

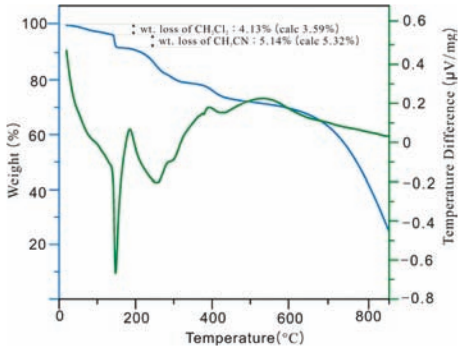

Figure 4. TGA/DTA curves of **2**.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) performed on **2** (Figure 4) shows a sharp weight loss of 5.14% at around 140 °C corresponding to the loss of coordinated acetonitrile molecules (expected value 5.32%). The DTA curve also shows a sharp endothermic peak at the same temperature, which corresponds to heat absorption due to the loss of coordinated acetonitrile. The IR spectrum of **2** obtained after heating to 140 °C also confirms the removal of acetonitrile by the disappearance of the absorption peak at 2366 cm^{-1} (ν_{CN}). The initial weight loss completed at about 130 °C corresponds to uncoordinated dichloromethane in the lattice. Because single crystallinity was not retained during the removal process of coordinated acetonitrile by heating, further structural studies were not available.

In summary, homo- and heteronuclear coordination polymers with different networking motifs were prepared from one-pot reactions of a thiaoxamacrocycle with CuI in the absence and presence of KI. The KI added with CuI induced not only the endocyclic complexation of a K^I ion but also the rearrangement of a copper(I) iodide cluster by coordination of an I ion. On the basis of this work, further synthesis and structural and photophysical studies of novel heteronuclear coordination polymers are also underway in our laboratory.

CCDC 787695 (**1**) and CCDC 787696 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Synthetic procedures, analytical data, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] (a) He, X.; Noll, B. C.; Beatty, A.; Mulvey, R. E.; Henderson, K. W. *J. Am. Chem. Soc.* **2004**, *126*, 7444. (b) Fehlhammer, W. P.; Schrolkamp, S.; Hoyer, M.; Hartl, H.; Beck, W. *Z. Anorg. Allg. Chem.* **2005**, *631*, 3025. (c) Li, D.-C.; Du, M.-X.; Dou, J.-M.; Wang, D.-Q. *Z. Anorg. Allg. Chem.* **2005**, *631*, 178. (d) Cole, M. L.; Jones, C.; Junk, P. C. *J. Chem. Soc., Dalton Trans.* **2002**, 896. (e) Röttgers, T.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1976. (f) Röttgers, T.; Sheldrick, W. S. *J. Solid State Chem.* **2000**, *152*, 271.