doi:10.1246/cl.2012.334

Published on the web February 29, 2012

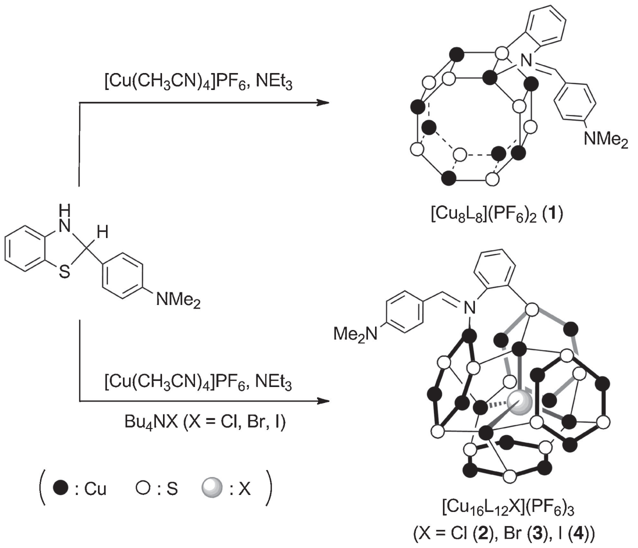
Halide-controlled Construction and Structural Determination of a Series of Thiolato-bridged 16-Nuclear Copper(I) Clusters from Benzothiazoline

Yusuke Takino,[1] Nobuto Yoshinari,[1] Kiyoshi Tsuge,[2] Tatsuya Kawamoto,[3] and Takumi Konno*[1]
[1]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*
[2]*Department of Chemistry, Graduate School of Science and Engineering, University of Toyama,*
3190 Gofuku, Toyama 930-8555
[3]*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293*

(Received December 5, 2011; CL-111164; E-mail: konno@chem.sci.osaka-u.ac.jp)

Treatment of $[Cu(CH_3CN)_4]^+$ with 2-(4-dimethylaminophenyl)benzothiazoline in the presence of halide ions ($X = Cl^-$, Br^-, and I^-) gave $[Cu_{16}L_{12}X]^{3+}$ ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$) with a spherical $Cu_{16}S_{12}$ structure, while similar treatment in the absence of halide ions afforded $[Cu_8L_8]^{2+}$ with a cyclic Cu_8S_8 structure.

Over the past decades, thiolato-bridged multinuclear copper species have attracted considerable attention not only in the field of inorganic chemistry because of their intriguing structural versatility,[1] but also in the field of biological chemistry because of their relevance to structural models of copper-containing metalloenzymes.[2] To date, a large number of thiolato-bridged copper compounds with different nuclearities and electronic states have been prepared,[3,4] thanks to the diversity of coordination geometries and oxidation states for copper ions in combination with the diversity of bridging modes for thiolate groups. In some cases, the structures of this class of compounds have been controlled by external factors such as reaction ratios, ancillary ligands, and reaction solvents.[3] However, this is almost limited to low-nuclearity systems, and the finding of an external factor that leads to the rational construction of copper species with a high nuclearity is a current concern in thiolato-bridged copper chemistry. In our successive study on the reactivity of 2-substituted benzothiazolines toward transition-metal ions,[5] we have recently found that the reaction of copper(II) with 2 equivalents of 2-(4-dimethylaminophenyl)benzothiazoline affords a unique thiolato-bridged 8-nuclear copper complex, $[Cu_8L_8]^+$ ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$), which is converted to $[Cu_8L_8]^{2+}$ under aerobic conditions with retention of its cyclic-ladder Cu_8S_8 core structure.[6] In this reaction, 2-(4-dimethylaminophenyl)benzothiazoline acts not only as a precursor of ligand but also as a reducing agent of copper(II) to produce $[Cu_8L_8]^+$, in which the copper ions virtually exit as a +1 oxidation state with one electron being delocalized over the Cu_8S_8 core. This is indicative of the possible formation of $[Cu_8L_8]^{+/2+}$ from the reaction of copper(I) with equimolar 2-(4-dimethylaminophenyl)benzothiazoline, which prompted us to investigate this 1:1 reaction. While this reaction gave $[Cu_8L_8]^{2+}$ as a major product, we found the formation of a novel thiolato-bridged 16-nuclear copper(I) cluster with a central Cl^- ion as a minor product when chloroform was used as a solvent. Notably, this compound was effectively formed by adding Cl^- ions. In this paper, we report on these intriguing results, together with the preparation and structural characterization of analogous 16-nuclear copper(I) compounds with a central Br^- or I^- ion, which demonstrate for the first time that thiolato-bridged copper structures are rationally expanded by halide ions (Scheme 1).[7]



Scheme 1. Synthetic routes of **1**, **2**, **3**, and **4**.

The reaction of $[Cu(CH_3CN)_4]PF_6$ in acetonitrile with equimolar 2-(4-dimethylaminophenyl)benzothiazoline in chloroform gave a brown solid, which was crystallized from a mixture of methanol and chloroform to produce black crystals **1** in a satisfactory yield.[8,9] Compound **1** was confidently assigned as a PF_6^- salt of $[Cu_8L_8]^{2+}$, based on its absorption spectrum that exhibits a characteristic intense near-infrared band at around 1220 nm,[6] besides its ^1H NMR spectrum (Figure 1a) and elemental analysis.[10] On the other hand, a similar crystallization procedure from chloroform led to the production of red microcrystals **2** as a minor product, together with black crystals of **1**.[8] When the mixture of **1** and **2** was treated with methanol, only **2** was dissolved to give a dark red solution, from which single crystals of **2**·6MeOH suitable for X-ray crystallography were obtained.[8]

The structure of **2**·6MeOH, determined by X-ray analysis, revealed the presence of a twelfth of complex cation and a quarter of PF_6^- anion, besides solvated methanol in the asymmetric unit.[11] The entire complex-cation of **2** ($[Cu_{16}L_{12}Cl]^{3+}$) contains sixteen Cu atoms, twelve iminothiolate ligands ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$), and one central Cl^- ion. Considering the total charge of the complex-cation and the monoanionic nature of the iminothiolate ligand, each Cu atom in **2** is assigned to have a +1 oxidation state. As shown in

© 2012 The Chemical Society of Japan

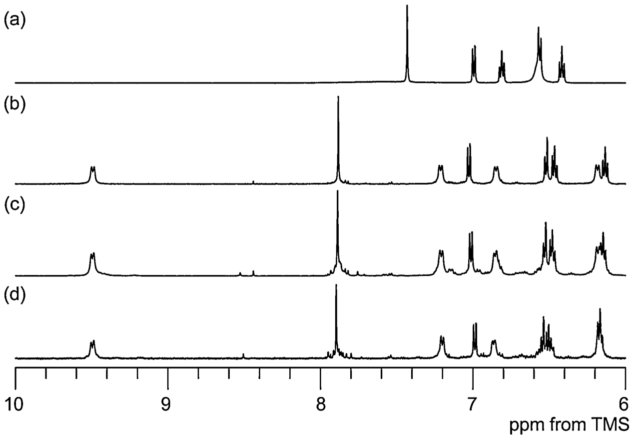


Figure 1. ^{1}H NMR spectra of (a) **1** in 1,2-dichloroethane-d_4 and (b) **2**, (c) **3**, and (d) **4** in acetonitrile-d_3 at 0 °C (aromatic proton region).

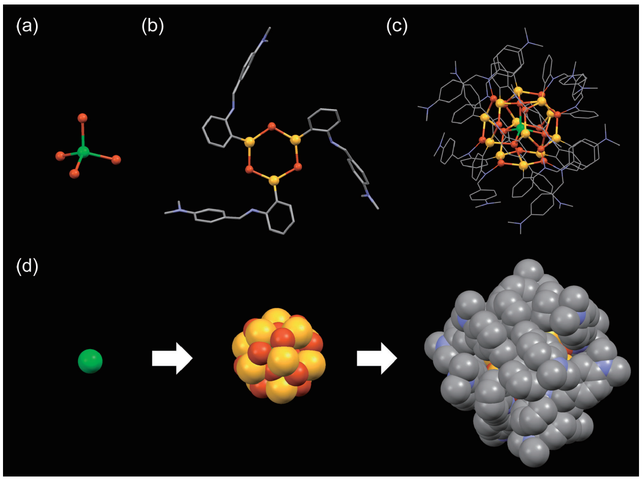


Figure 2. Perspective views of (a) the tetrahedral $[Cu_4Cl]^{3+}$ core, (b) the hexagonal $[Cu_3L_3]$ ring, (c) the overall structure of $[Cu_{16}L_{12}Cl]^{3+}$, and (d) the double-layer structure accommodating a chloride ion in **2**. H atoms are omitted for clarity. Cu: brown, S: yellow, Cl: green, C: gray, N: blue.

Figure 2, the complex-cation consists of a tetrahedral $[Cu_4Cl]^{3+}$ core, in which a central Cl^- ion is bound by four Cu atoms in a tetrahedral geometry (Cu–Cl = 2.4991(5) Å), and four outer $[Cu_3L_3]$ units, in which three Cu atoms are alternately bridged by three S atoms from three L ligands to form a hexagonal ring (av. Cu–S = 2.290(14) Å). The four $[Cu_3L_3]$ ring-units, which are connected with each other through Cu–N bonds (2.004(2) Å), are in a tetrahedral arrangement, and they bind to the tetrahedral $[Cu_4Cl]^{3+}$ core through Cu–S bonds (2.3287(6) Å). This binding fashion completes a unique *T* symmetric cluster structure with a diameter of ca. 21 Å, in which a spherical $Cu_{16}S_{12}$ layer that accommodates a Cl^- ion is covered by an organic layer. As far as we know, **2** is the first structurally characterized thiolato-bridged copper(I) cluster having a 16 nuclearity.[12] Note that there exist six sets of intramolecular π–π interaction (3.63(2) Å) between *N*,*S*-bridging phenyl rings and pendent phenyl rings in the organic layer,[13] which appears to support this spherical structure. In **2**, each L ligand bridges four Cu atoms using μ_3-thiolate and μ_1-imine groups. The coordination geometry of Cu^I atoms in **2** is best described as distorted ClS_3 trigonal pyramid and NS_2 trigonal plane for those in the tetrahedral $[Cu_4Cl]^{3+}$ core and the $[Cu_3L_3]$ ring-units, respectively.

Unlike the absorption spectrum of **1**, no near-infrared band is observed in the absorption spectrum of **2** in acetonitrile. This is compatible with the assignment of the +1 oxidation state for all Cu atoms in **2**, with the lack of electron(s) delocalized over the S-bridged core structure.[6] In the ^{1}H NMR spectrum in acetonitrile-d_3, **2** exhibits a single set of signals (nine 1H aromatic and one 6H methyl proton signals) for twelve L ligands in the complex (Figure 1b), suggestive of the retention of the *T* symmetric structure found in the crystal.[8] Consistent with this, the ESI mass spectrum of **2** in acetonitrile gave a cluster of signals centered at m/z 1372, the calculated mass and the isotopic distribution of which match well with those for $[Cu_{16}L_{12}Cl]^{3+}$ (Figure S1).[8]

To check whether **2** is formed in preference to **1** in the presence of a sufficient amount of Cl^- ions, an acetonitrile solution of $[Cu(CH_3CN)_4]PF_6$ was treated with equimolar 2-(4-dimethylaminophenyl)benzothiazoline dissolved in chloroform in the presence of excess Bu_4NCl.[8] As a result, only a red powder of **2** was produced in a moderate yield from this solution.[14] In addition, **2** was obtained in a higher yield by the reaction of $[Cu(CH_3CN)_4]PF_6$ with 2-(4-dimethylaminophenyl)-benzothiazoline in a stoichiometric ratio of 4:3 in the presence of excess Bu_4NCl.[8] These results imply that a Cl^- ion acts as a template for the construction of the spherical $Cu_{16}S_{12}$ structure in **2**. The template effect due to Cl^- was confirmed by the ^{1}H NMR spectroscopy of the 4:3 reaction solution of $[Cu(CH_3CN)_4]PF_6$ and 2-(4-dimethylaminophenyl)benzothiazoline in methanol-d_4/acetonitrile-d_3. That is, the ^{1}H NMR spectrum before adding Bu_4NCl showed complicated, multiple proton signals, while a single set of signals for **2** appeared dominantly in the ^{1}H NMR spectrum after adding Bu_4NCl (Figure S2).[8]

When $[Cu(CH_3CN)_4]PF_6$ was treated with 2-(4-dimethylaminophenyl)benzothiazoline in a 4:3 ratio by adding Bu_4NBr or Bu_4NI, instead of Bu_4NCl, a reddish powder **3** or **4** was obtained in a reasonable yield.[8] The elemental analyses of **3** and **4** were in agreement with the formulas for $[Cu_{16}L_{12}X]^{3+}$ (X = Br for **3**, X = I for **4**),[15,16] and the presence of Br or I atoms in **3** or **4** was confirmed by the X-ray fluorescence spectrometry. In addition, the ^{1}H NMR spectrum of each of **3** and **4** in acetonitrile-d_3 gives a single set of signals, the chemical shifts of which are very similar to those for **2** (Figures 1c and 1d). Judging from these results, together with the absence of intense near-infrared bands in the absorption spectra, **3** and **4** are assigned a spherical copper(I) structure analogous to **2**. This was unambiguously confirmed by single-crystal X-ray analyses.[17,18] The overall structure of the complex-cation ($[Cu_{16}L_{12}X]^{3+}$) in each of **3** and **4** is very similar to that in **2**, except the presence of Br^- or I^- in place of Cl^- in **2** (Figures 3 and S3).[8] As expected, the Cu–X bond distances increase in the order $X = Cl^-$ (2.4991(5) Å) < Br^- (2.5819(4) Å) < I^- (2.6589(8) Å). However, the differences are rather small relative to those in the ionic radius between the halide ions (Cl^- = 1.81 Å, Br^- = 1.96 Å, and I^- = 2.20 Å).[19] In addition, the distances between the central halide ion and the center of each Cu_3S_3 ring in **2** (3.007(1) Å), **3** (3.001(2) Å), and **4** (3.025(5) Å) are essentially the same. Thus, the size of the

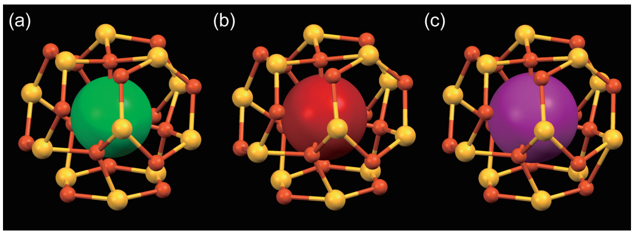


Figure 3. Perspective views of the $Cu_{16}S_{12}X$ core structure in (a) **2**, (b) **3**, and (c) **4**. Cu: brown, S: yellow, Cl: green, Br: red-brown, I: purple.

$Cu_{16}S_{12}$ sphere is little affected by the accommodated halide ion. This is most likely due to the outer organic layer, the size of which is predetermined by the multiple intramolecular π–π interactions.

In summary, we showed that 2-(4-dimethylaminophenyl)-benzothiazoline readily reacts with copper(I) ion in the presence of chloride ions to form the novel 16-nuclear copper(I) cluster having a central chloride ion, $[Cu_{16}L_{12}Cl]^{3+}$. This cluster was found to possess a unique spherical double-layer structure, in which the organic layer covers the inner $Cu_{16}S_{12}$ spherical framework. The presence of bromide or iodide ions afforded analogous spherical clusters with a central bromide or iodide ion. While a number of discrete multinuclear species that accommodate a halide ion in the center have been prepared,[1a,4a–4d,20] reports on the construction and structural determination of a series of multinuclear compounds with a chloride, bromide, or iodide ion are quite rare.[4d] Finally, it should be noted that a similar reaction in the absence of halide ions gave only the cyclic 8-nuclear copper cluster, $[Cu_8L_8]^{2+}$. This demonstrates that halide ions act as a template for the construction of $[Cu_{16}L_{12}X]^{3+}$ and that the 16- and 8-nuclear copper structures are controlled by the presence/absence of halide ions. Halide-controlled construction of thiolato-bridged copper clusters with use of other benzothiazolines is currently underway in our laboratory.

This work was supported in part by Grants-in-Aids for Science Research (No. 23107517) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References and Notes

1 a) P. J. Blower, J. R. Dilworth, *Coord. Chem. Rev.* **1987**, *76*, 121. b) S. Mandal, G. Das, R. Singh, R. Shukla, P. K. Bharadwaj, *Coord. Chem. Rev.* **1997**, *160*, 191. c) C. W. Liu, R. J. Staples, J. P. Fackler, *Coord. Chem. Rev.* **1998**, *174*, 147. d) J. T. York, I. Bar-Nahum, W. B. Tolman, *Inorg. Chim. Acta* **2008**, *361*, 885. e) Z.-N. Chen, N. Zhao, Y. Fan, J. Ni, *Coord. Chem. Rev.* **2009**, *253*, 1.

2 a) M. J. Stillman, *Coord. Chem. Rev.* **1995**, *144*, 461. b) J. Chan, Z. Huang, M. E. Merrifield, M. T. Salgado, M. J. Stillman, *Coord. Chem. Rev.* **2002**, *233–234*, 319. c) D. E. K. Sutherland, M. J. Stillman, *Metallomics* **2011**, *3*, 444.

3 a) M. D. Janssen, J. G. Donkervoort, S. B. van Berlekom, A. L. Spek, D. M. Grove, G. van Koten, *Inorg. Chem.* **1996**, *35*, 4752. b) Z. Li, S. Du, X. Wu, *Dalton Trans.* **2004**, 2438. c) O. Fuhr, L. Fernandez-Recio, D. Fenske, *Eur. J. Inorg. Chem.* **2005**, 2306. d) S. Schneider, J. A. S. Roberts, M. R. Salata, T. J. Marks, *Angew. Chem., Int. Ed.* **2006**, *45*, 1733. e) S. Schneider, A. Dzudza, G. Raudaschl-Sieber, T. J. Marks, *Chem. Mater.* **2007**, *19*, 2768. f) B. K. Maiti, K. Pal, S. Sarkar, *Eur. J. Inorg. Chem.* **2007**, 5548.

4 a) N. Assavathorn, R. P. Davies, A. J. P. White, *Polyhedron* **2008**, *27*, 992. b) N. Yoshinari, K. Tatsumi, A. Igashira-Kamiyama, T. Konno, *Chem.—Eur. J.* **2010**, *16*, 14252. c) N. Yoshinari, A. Igashira-Kamiyama, T. Konno, *Chem.—Eur. J.* **2010**, *16*, 14247. d) N. Yoshinari, T. Konno, *Dalton Trans.* **2011**, *40*, 12191. e) A. Neuba, U. Flörke, W. Meyer-Klaucke, M. Salomone-Stagni, E. Bill, E. Bothe, P. Höfer, G. Henkel, *Angew. Chem., Int. Ed.* **2011**, *50*, 4503.

5 a) T. Kawamoto, K. Takeda, M. Nishiwaki, T. Aridomi, T. Konno, *Inorg. Chem.* **2007**, *46*, 4239. b) T. Kawamoto, M. Nishiwaki, Y. Tsunekawa, K. Nozaki, T. Konno, *Inorg. Chem.* **2008**, *47*, 3095. c) T. Kawamoto, Y. Takino, K. Sakoda, T. Konno, *Chem. Lett.* **2010**, *39*, 1264. d) Y. Takino, K. Tsuge, A. Igashira-Kamiyama, T. Kawamoto, T. Konno, *Chem.—Asian J.* **2011**, *6*, 2931.

6 T. Kawamoto, M. Nishiwaki, M. Nishijima, K. Nozaki, A. Igashira-Kamiyama, T. Konno, *Chem.—Eur. J.* **2008**, *14*, 9842.

7 Halide-templated construction of S-bridged copper(I) complexes with dithiophosphates has been reported. a) C. W. Liu, M. D. Irwin, A. A. Mohamed, J. P. Fackler, Jr., *Inorg. Chim. Acta* **2004**, *357*, 3950. b) B.-J. Liaw, T. S. Lobana, Y.-W. Lin, J.-C. Wang, C. W. Liu, *Inorg. Chem.* **2005**, *44*, 9921.

8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Calcd for **1**$\cdot$2$CHCl_3$: C, 47.58; H, 3.99; N, 7.28%. Found: C, 47.63; H, 4.09; N, 7.36%. Yield: 75%.

10 The exclusive production of **1** by the crystallization from methanol/chloroform is likely in part due to the high solubility of **2** in methanol, as well as the lack of Cl^- ions in this solution.

11 Crystal data for **2**$\cdot$6MeOH, Cubic, $Fd\bar{3}c$, $a = 43.5328(8)$ Å, $V = 82499(5)$ Å^3, $Z = 16$, $T = 200(2)$ K, $D_{calcd} = 1.528$ g cm^{-3}, 188243 reflections measured, 3942 independent ($R_{int} = 0.136$), $R1 = 0.056$ ($I > 2\sigma(I)$), $wR2 = 0.165$ (all data).[21,22] CCDC-855296.

12 A similar spherical $Cu_{16}S_{12}$ framework, which possesses a Se^{2-} ion in the center, has been found in $[Cu_{20}Se(SPh)_{12}(OAc)_6(PPh_3)_4]$.[3c]

13 C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525.

14 Calcd for **2**$\cdot$7H_2O: C, 46.22; H, 4.18; N, 7.19%. Found: C, 46.19; H, 4.14; N, 7.20%. Yield: 40%.

15 Calcd for **3**$\cdot$9H_2O: C, 45.44; H, 4.19; N, 7.07%. Found: C, 45.47; H, 3.91; N, 7.03%. Yield: 74%.

16 Calcd for **4**$\cdot$2CuI$\cdot$2H_2O: C, 42.73; H, 3.67; N, 6.64%. Found: C, 42.44; H, 3.64; N, 6.60%. Yield: 67%.

17 Crystal data for **3**$\cdot$6MeOH, Cubic, $Fd\bar{3}c$, $a = 44.0618(6)$ Å, $V = 85543(2)$ Å^3, $Z = 16$, $T = 200(2)$ K, $D_{calcd} = 1.487$ g cm^{-3}, 215493 reflections measured, 4090 independent ($R_{int} = 0.058$), $R1 = 0.041$ ($I > 2\sigma(I)$), $wR2 = 0.139$ (all data).[21,22] CCDC-855297.

18 Crystal data for **4**$\cdot$6MeOH, Cubic, $Fd\bar{3}c$, $a = 44.2098(16)$ Å, $V = 86408(9)$ Å^3, $Z = 16$, $T = 200(2)$ K, $D_{calcd} = 1.487$ g cm^{-3}, 196933 reflections measured, 4139 independent ($R_{int} = 0.149$), $R1 = 0.070$ ($I > 2\sigma(I)$), $wR2 = 0.208$ (all data).[21,22] CCDC-855298.

19 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751.

20 a) T. S. Lobana, J.-C. Wang, C. W. Liu, *Coord. Chem. Rev.* **2007**, *251*, 91. b) R. Vilar, *Eur. J. Inorg. Chem.* **2008**, 357.

21 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.

22 C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *Nihon Kessho Gakkaishi* **2009**, *51*, 218.