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(ベンゾチアゾリンから誘導合成される金(I)、銀(I)、および銅(I)多核錯体の構造研究)

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Contents

Chapter I. General Introduction.

Gold, silver, and copper that belong to group 11 are the oldest known elements and are utilized as currency, embellishment, and industrial raw materials in their elemental state due to the great chemical stability. In coordination chemistry, the +I oxidation state of these elements, which has a closed-shell d^{10} electronic state, has been intensively investigated over the past decades. Since the d^{10} electronic state of the metal center eliminates the contribution due to the ligand-field stabilization energy (LFSE), metal complexes of Au^I, Ag^I, and Cu^I are generally less stable than those of other transition metal ions. On the other hand, the lack of LFSE allows these d^{10} metal complexes to adopt unique coordination geometries with a coordination number lower than 4.[1] Indeed, linear, bent, trigonal-planar, T-shape, Y-shape, trigonal-pyramidal, and tetrahedral geometries have been reported for these d^{10} metal complexes. It should be noted that this class of metal ions tends to bind to 'soft' donor groups (e.g. halides, thiolates, and phosphines) due to their softness, which is in contrast to 'hard' d^{10} metal ions of group 12 elements.[2]

In recent years, constructions of multinuclear complexes of d^{10} metal ions of group 11 elements have quickly developed by the use of bridging ligands. That is, a number of multinuclear complexes containing heterodimetallic cores, have been synthesized and their structures and photophysical, electrochemical, catalytic, and pharmacological properties have been investigated.[3,4] In such multinuclear systems, intramolecular interactions between d^{10} metal centers, so called 'd^{10}-d^{10} interactions', often contribute to their structures and functionalities.[4] However, the fine control of multinuclear structures for d^{10} metal complexes is still difficult even for a simple homometallic system because of the flexible coordination geometries of d^{10} metal ions and the unpredictability of d^{10}-d^{10} interactions. Thus, new methods that lead to the controlled construction of multinuclear structures are strongly required in this field even for heterometallic systems.

Thiolato-bridged metal complexes are among the most extensively studied multinuclear compounds, which is due to their structural relevance to the active sites of metalloproteins and due to their intriguing physical and chemical properties.[5] Considering the softness of d^{10} metal ions of group 11 elements, construction of their multinuclear structure with use of 'soft' thiolato sulfur donors is appropriate, and indeed, a number of this class of multinuclear complexes has appeared to date. From the viewpoint of structural chemistry, however, it is difficult to control the resulting S-bridged structures, especially in the flexible d^{10} metal systems, because thiolato groups can adopt various binding modes such as monodentate-S, μ_2-S, and μ_3-S. The use of multidentate chelating ligands containing both 'soft' thiolate and some 'hard' donor groups seems to be effective to remove this problem. This is because the binding of 'hard' donor groups to several coordination sites of metal ions can limit the formation of undesirable S-bridged structures to control nuclearity of the multinuclear complexes. Moreover, the difference in affinity between 'soft' and 'hard' donor groups can distinguish two different metal ions, leading to the rational construction of heterometallic multinuclear complexes.

It is well known that iminothiophenolates act as an effective chelating ligand having 'soft' thiophenolate sulfur and 'hard' imine nitrogen donor atoms. However, in many cases, the isolation of iminothiophenolates is difficult because they tend to be quickly converted to undesirable byproducts, such as dithiocins.[6] Therefore, *In-situ* prepared iminothiophenolates are often used to react with metal ions. The iminothiophenolate ligands can be classified into two types with respect to the position of N atoms (Chart 1). One is (iminomethyl)benzenethiolates, which are prepared from the condensation reactions of 2-mercaptobenzaldehydes and amines (Type A). The other is the (ylideneamino)benzenethiolates, which are derived from the reactions of 2-aminothiophenols and aldehydes (Type B). To date, a few hundreds of mononuclear and multinuclear complexes with iminothiophenolate ligands for both types have been prepared and structurally characterized,[7-9] but examples of the d^{10} metal complexes of group 11 elements are very rare. Only three Cu^I complexes with type A ligands, $[Cu_{2n}(\textit{iso-abt})_n]$ ($\textit{iso-abt} = C_6H_4(CH{=}NC_6H_4S)_2$; n = 2, 6)[8] and $[Cu_4L_2(CH_3CN)](PF_6)_2$ ($L = SC_6H_2Me(CH{=}N(CH_2)_3NMe_2)_2$),[9] have been reported so far. It has been recognized that 2-substituted benzothiazolines can convent to the latter type through a C-S bond cleavage without the formation of byproducts, which is advantageous for the synthesis of their metal complexes. Until now, the reactivity of 2-substituted benzothiazolines with octahedral, tetrahedral, and square-planar transition metal ions have been investigated.[10-15] For example, the reactions of 2-substituted benzothiazolines with $[Ir_2(\mu_2\text{-}Cl)_2(ppy)_4]$ afforded mononuclear Ir^{III} complexes, $[Ir(L)(ppy)_2]$ (Hppy = 2-phenylpyridine, L = (ylideneamino)benzenethiolates), which show unique reversible *E*/*Z* isomerization around a C=N bond induced by light and heat in the solid state.[10] The reactions with tetrahedral Zn^{II} ion led to photo-emissive mononuclear Zn^{II} complexes, $[M(L)_2]$, the luminescence energy of which is highly dependent on the substituent groups on the pendant phenyl rings of L.[11] Furthermore, the reactions with square-planar Ni^{II} ion gave mononuclear complexes, $[Ni(L)_2]$, which show cis/trans isomerism that is controlled by the steric constraint of the substituent groups on the pendant phenyl rings of iminothiophenolates.[12] Finally, the reactions with square-planar Cu^{II} ion induced redox between Cu^{II} and benzothiazolines to give μ_3-thiolate-bridged octacopper(I) complexes, $[Cu_8L_8]^{n+}$ (n= 0, 1, 2), in which dicationic, monocationic, and neutral oxidation states are interconvertible to one another with retention of the cyclic $\{Cu_8S_8\}$ core structure.[13] However, the reactivities of benzothiazolines toward linear-type metal ions have been unexplored to date.

In this thesis, the reactivities of benzothiazolines toward group 11 metal ions with the +1 oxidation state, which tend to adopt coordination geometries with lower coordination numbers, have been investigated. In Chapter II, the reactions of several 2-substituted benzothiazolines having different substituent groups on a pendant phenyl group with each of Au^I, Ag^I, and Cu^I ions, together with the structural characterization of the resulting homometallic d^{10} complexes are described. In addition, the structural difference among these complexes is discussed in terms of metal source, substituent groups, and template ions. In Chapter III, the reactivity of 2-substituted benzothiazolines toward each of mixtures of Au^I and Ag^I, Au^I and Cu^I, and Ag^I and Cu^I is reported. For the resulting heterometallic complexes, the arrangement of metal ions in the molecular structures is discussed in detail. The structures of the compounds reported in this thesis were characterized by ^1H NMR, electronic absorption, IR, and Electrospray ionization (ESI) mass spectra, along with single-crystal X-ray analysis. The ligands used in this study are summarized in Scheme 1.

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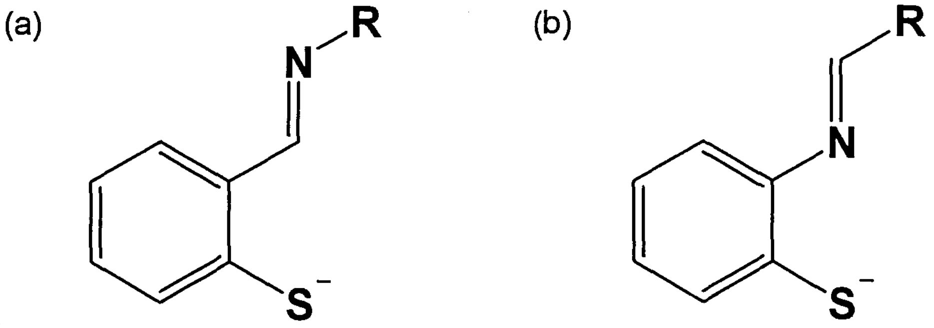
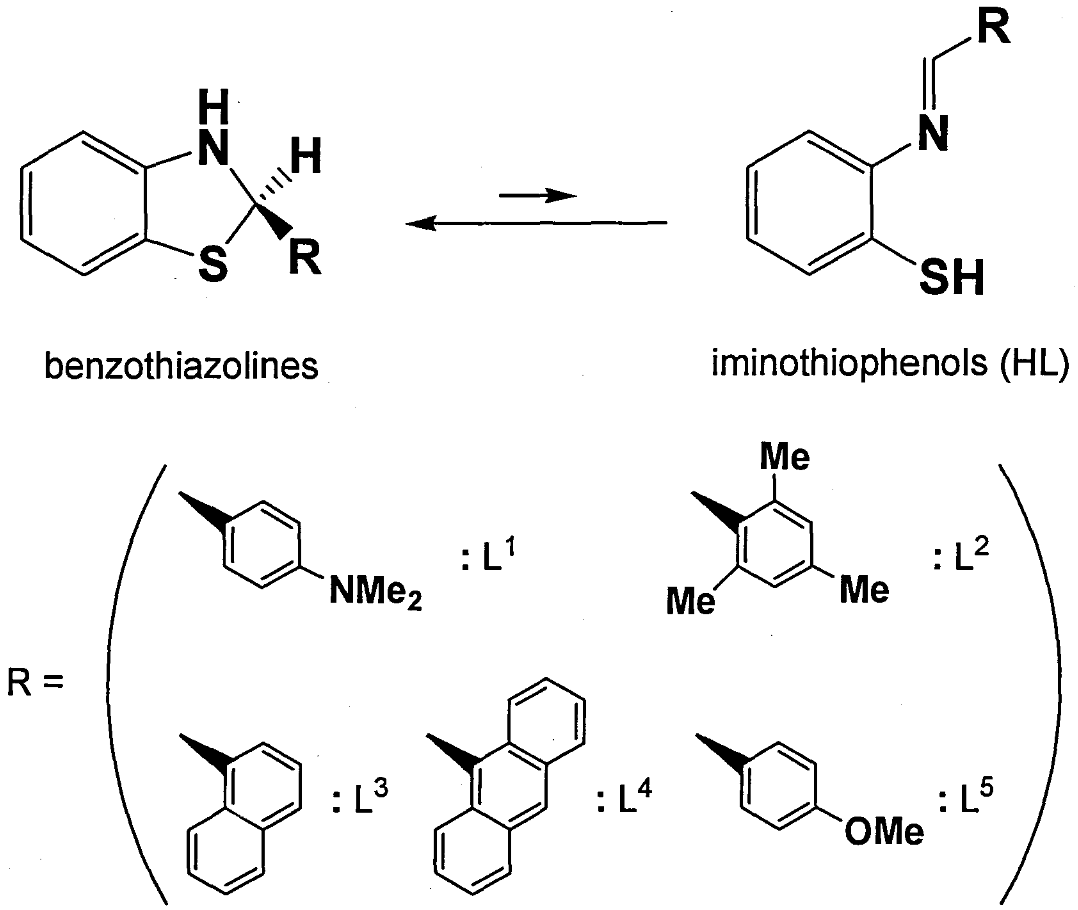


(iminomethyl)benzenethiolates
(Type A)

(ylideneamino)benzenethiolates
(Type B)

Chart 1. Two types of iminothiophenolate ligands.



Scheme 1. Equilibrium between benzothiazolines and iminothiophenols (HL).

Chapter II.
Homometallic Complexes Derived from Benzothiazolines.

II-1. Introduction.

As mentioned in Chapter I, the d^{10} ions of group 11 elements can adopt various coordination geometries with coordination numbers lower than 4 because of the lack of the ligand-field stabilization energy. In particular, a linear geometry, which is rarely found in other transition metal ions, is often observed for this class of metal ions.[1] A broad trend of the coordination geometries among Au^I, Ag^I, and Cu^I, has been reviewed.[2,3] For Au^I ion, it has been shown that the strong relativistic effect promotes the formation of linear-type complexes, while trigonal-planar and tetrahedral Au^I complexes have been rarely observed.[1,4] On the other hand, trigonal-planar and tetrahedral complexes are more dominant than linear one for the Cu^I complexes because the relativistic effect of Cu^I ion is weaker than that of Au^I ion. Ag^I ion takes a mean position between Au^I and Cu^I, adopting flexible coordination geometries ranging from linear to tetrahedral. However, the coordination geometries of this class of metal ions are not strict and are highly dependent on the kind of ligands. Therefore, the investigation of coordination behavior of new ligands to d^{10} metal ions is desirable.

While no systematic investigation on the coordination behavior of iminothiophenolates to a series of group 11 metal ions (Au^I, Ag^I, and Cu^I) has been reported, the reactivities of either thiophenolates or imines with these metal ions have been extensively investigated to date.[2,3,5-10] Since thiophenolate ligands are classified in a 'soft' base, they strongly bind to all of group 11 metal ions, forming S-bridged multinuclear structures.[5-7] On the other hand, imine ligands are classified in a 'hard' base, and thus, a number of researches on the coordination behavior of these ligands to relatively hard Ag^I and Cu^I ions have been reported,[8,9] while few Au^I complex with these ligands have been reported.[10] Considering these results, it is expected that the reactions of iminothiophenolate ligands derived from benzothiazolines with each of Au^I, Ag^I, and Cu^I ions commonly form S-bridged multinuclear complexes, where the coordination of imino groups occurs only to Ag^I and Cu^I ions.

In this chapter, the coordination behavior of iminothiophenolate ligands toward a series of d^{10} metal ions of group 11 elements were investigated through the reactions of 2-substituted benzothiazolines with each of Au^I, Ag^I, and Cu^I ions. These reactions gave thiolato-bridged multinuclear complexes, which were characterized by ^1H NMR, electronic absorption, IR, and ESI mass spectra, along with single-crystal X-ray analyses. The substituent effect of ligands and template effect of halide ions on the resulting multinuclear structures were also discussed.

II-2. Experimental section.

II-2-1. General procedure.

Initial part of the reactions containing benzothiazolines were carried out using standard Schlenk techniques under an atmosphere of nitrogen, while other treatments and measurements were done in air.

II-2-2. Materials.

Benzothiazolines were prepared by the methods of the literature.[11] The starting materials, [AuCl(tht)][12] (tht = tetrahydrothiophene) and $[Cu(CH_3CN)_4]PF_6$,[13] were prepared by the methods of the literature. The reagents were of the commercial grade and used without further purification.

II-2-3. Physical measurements.

The Infrared spectra were measured with a JASCO FT/IR-4100 infrared spectrophotometer by using KBr pellet. The ^{1}H NMR spectra were recorded on a JEOL ECA-500 (500 MHz) and a JNM-GSX-400 (400 MHz) instruments, respectively, under a controlled temperature (30°C or 0°C) using tetramethylsilane (TMS) as the internal standard (δ 0 ppm). The electronic absorption and diffuse reflectance spectra were recorded on a JASCO V-570 spectrophotometer. The elemental analyses (C, H, N) were performed at Osaka University. Electrospray ionization (ESI) mass spectra were recorded on a JASCO API LC-TOF/MS instrument. Single-crystal X-ray diffraction experiments were performed on a Rigaku RAXIS-RAPID imaging plate area detector with a graphite monochromated Mo-Kα radiation at 200 K. The intensity data were collected by the ω scan technique and were empirically corrected for absorption. The structures were solved by direct methods and were refined with full-matrix least-squares on F^2. Hydrogen atoms were placed at calculated positions but were not refined. All calculations were performed using Yadokari-XG 2009 software package,[14] except the refinements that were performed using SHELXL-97.[15]

II-2-4. Preparation of homometallic complexes.

II-2-4-1. Au^{I} complexes 1 and 2.

(a) Synthesis of [Au$_4$(L^1)$_4$] (1).

To a yellow solution of 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol) in 30 mL of $CHCl_3$ was sequentially added Et_3N (0.04 g, 0.40 mmol) and [AuCl(tht)] (0.13 g, 0.39 mmol) in 5 mL of $CHCl_3$. The mixture was stirred at room temperature for 30 min, concentrated to ca. 5 mL, and then n-C_6H_{14} was added to it. The resulting yellow powder of **1** was collected by filtration and washed with EtOH. Yield: 0.16 g, 85%. Anal. Found: C, 37.91; H, 3.24; N, 5.86%. Calcd for [Au$_4$(L^1)$_4$]·$CHCl_3$: C, 37.99; H, 3.19; N, 5.81%. ^{1}H NMR (500 MHz, $CDCl_3$, 30°C): δ 8.04 (1H, s, C*H*=N), 7.67 (2H, d, C*H* of pendant-Ph), 7.61 (1H, d, C*H* of N,S-Ph), 7.12 (1H, t, C*H* of N,S-Ph), 6.89 (1H, t, C*H* of N,S-Ph), 6.79 (1H, d, C*H* of N,S-Ph), 6.49 (2H, d, C*H* of pendant-Ph), 2.96 (6H, s, CH_3). Single crystals of **1** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the yellow reaction solution.

(b) Synthesis of [Au$_4$(L^2)$_4$] (2).

To a pale yellow solution of 2-(2,4,6-trimethylphenyl)benzothiazoline (0.25 g, 1.0 mmol) in 10 mL of $CHCl_3$ was sequentially added Et_3N (0.10 g, 1.0 mmol) and [AuCl(tht)] (0.31 g, 1.0 mmol) in 5 mL of $CHCl_3$. The mixture was stirred at room temperature for 1 h, concentrated to a small volume, and then n-C_6H_{14} was added to it. The resulting pale yellow powder of **2** was collected by filtration and washed with EtOH. Yield: 0.35 g, 79%. Anal. Found: C, 42.43; H, 3.45; N, 3.03%. Calcd for [Au$_4$(L^2)$_4$]: C, 42.58; H, 3.57; N, 3.10%. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 8.54 (1H, s, C*H*=N), 7.66 (1H, d, C*H* of N,S-Ph), 7.16 (1H, t, C*H* of N,S-Ph), 6.92 (1H, t, C*H* of N,S-Ph), 6.75-6.70 (3H, m, C*H* of pendant-Ph and N,S-Ph), 2.49 (6H, s, CH_3) 2.24 (3H, s, CH_3). Single crystals of **2** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a solution of **2** in $CHCl_3$.

II-2-4-2. Ag^I complexes 3-7.

(a) Synthesis of $[Ag_4(L^1)_4]$ (3).

To a yellow solution of 2-(4-dimethylaminophenyl)benzothiazoline (1.0 g, 3.9 mmol) in 30 mL of $CHCl_3$ was sequentially added Et_3N (0.40 g, 4.0 mmol) and silver(I) perchlorate (0.81 g, 3.9 mmol) in 5 mL of EtOH. After the mixture was stirred at room temperature for 30 min in the dark, 100 mL of EtOH was added to it. The resulting yellow powder of **3** was collected by filtration and washed with EtOH. Yield: 1.3 g, 88%. Anal. Found: C, 47.84; H, 3.97; N, 7.54%. Calcd for $[Ag_4(L^1)_4]\cdot 0.5CHCl_3$: C, 48.04; H, 4.03; N, 7.41%. ^{1}H NMR (500 MHz, $CDCl_3$, 30°C): δ 7.80 (1H, s, C*H*=N), 7.72 (2H, d, C*H* of pendant-Ph), 7.56 (1H, d, C*H* of N,S-Ph), 7.04 (1H, t, C*H* of N,S-Ph), 6.88 (1H, t, C*H* of N,S-Ph), 6.75 (1H, d, C*H* of N,S-Ph), 6.30 (2H, d, C*H* of pendant-Ph), 3.01 (6H, s, CH_3). ^{1}H NMR (500 MHz, $CDCl_3$, 0°C): δ 7.79 (1H, s, C*H*=N), 7.74 (2H, d, C*H* of pendant-Ph), 7.56 (1H, d, C*H* of N,S-Ph), 7.05 (1H, t, C*H* of N,S-Ph), 6.88 (1H, t, C*H* of N,S-Ph), 6.76 (1H, d, C*H* of N,S-Ph), 6.29 (2H, d, C*H* of pendant-Ph), 3.03 (6H, s, CH_3). Single crystals of **3** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the reaction solution.

(b) Synthesis of $[Ag_4(L^2)_4]$ (4).

To a pale yellow solution of 2-(2,4,6-trimethylphenyl)benzothiazoline (0.26 g, 1.0 mmol) in 10 mL of $CHCl_3$ was added silver(I) acetate (0.17 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h in the dark. After a small amount of precipitate was filtered off, 20 mL of n-C_6H_{14} was added to the filtrate, followed by concentrated to a small volume. The resulting yellow powder of **4** was collected by filtration and washed with EtOH. Yield: 0.35 g, 94%. Anal. Found: C, 51.76; H, 4.25; N, 3.83%. Calcd for $[Ag_4(L^2)_4]\cdot 0.4CHCl_3$: C, 51.68; H, 4.34; N, 3.74%. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 8.47 (1H, s, C*H*=N), 7.05-7.00 (2H, m, C*H* of N,S-Ph), 6.88 (1H, t, C*H* of N,S-Ph), 6.85-6.75 (3H, m, C*H* of pendant-Ph and N,S-Ph), 2.33 (6H, s, CH_3), 2.31 (3H, s, CH_3). Single crystals of **4** suitable for X-ray analysis were obtained by the slow diffusion of diethyl ether into a solution of **4** in $CHCl_3$.

(c) Synthesis of $[Ag_4(L^3)_4]$ (5).

To a light yellow solution of 2-(1-naphthyl)benzothiazoline (0.06 g, 0.24 mmol) in 15 ml of $CHCl_3$ was added silver(I) acetate (0.04 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 30 min in the dark. The reaction solution was added n-C_6H_{14} as a poor solvent. The resulting pale yellow powder of **5** was collected by filtration and washed with EtOH. Yield: 86 mg, 79%. Anal. Found: C, 47.01; H, 2.72; N, 3.17%. Calcd for $[Ag_4(L^3)_4]\cdot 2.75CHCl_3$: C, 46.97; H, 2.83; N, 3.10%. Single crystals of **5** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the yellow reaction solution.

(d) Synthesis of $[Ag_4(L^4)_4]$ (6).

To a light yellow solution of 2-(9-anthracenyl)benzothiazoline (0.10 g, 0.31 mmol) in 15 ml of $CHCl_3$ was added silver(I) acetate (0.04 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 1 h, and then the resulting yellow powder of **6** was collected by filtration and washed with $CHCl_3$. Yield: 90 mg, 88%. Anal. Found: C, 59.12; H, 3.36; N, 3.35%. Calcd for $[Ag_4(L^4)_4]\cdot 0.2CHCl_3$: C, 59.32; H, 3.32; N, 3.29%. Single crystals of **6** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the yellow reaction solution.

(e) Synthesis of $[Ag_4(L^5)_4]$ (7).

To a light yellow solution of 2-(4-methoxyphenyl)benzothiazoline (0.06 g, 0.24 mmol) in 15 ml of $CHCl_3$ was added silver(I) acetate (0.04 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 30 min in the dark. After filtration, n-C_6H_{14} was added to the filtrate as a poor solvent. The resulting pale yellow powder of 7 was collected by filtration and washed with EtOH. Yield: 65 mg, 69%. Anal. Found: C, 43.75; H, 3.25; N, 3.65%. Calcd for $[Ag_4(L^5)_4]\cdot 1.5CHCl_3$: C, 43.72; H, 3.16; N, 3.55%. Single crystals of 7 suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the yellow reaction solution.

II-2-4-3. Cu^I complexes 8-12.

(a) Synthesis of $[Cu_{10}(L^1)_9]PF_6$ (8).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.39 mmol) in 5 mL of CH_3CN was added a mixture of 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol) and Et_3N (0.04 g, 0.40 mmol) in 10 mL of MeOH. The reaction mixture was stirred at room temperature for 5 min, and the resulting red-orange powder of **8** was collected by filtration. Yield: 0.12 g, 97%. Anal. Found: C, 50.90; H, 4.51; N, 7.96%. Calcd for $[Cu_{10}(L^1)_9]PF_6\cdot6H_2O$: C, 50.88; H, 4.65; N, 7.91%. IR (KBr; cm^{-1}): 843 (PF_6^-), 558 (PF_6^-). ^1H NMR (500 MHz, CD_3CN, 30°C): δ 8.49 (1H, s, C*H*=N), 7.69 (2H, d, C*H* of pendant-Ph), 7.65 (1H, d, C*H* of N,S-Ph), 7.64 (2H, d, C*H* of pendant-Ph), 7.22 (2H, br, C*H* of pendant-Ph), 7.11 (1H, d, C*H* of N,S-Ph), 7.07 (1H, t, C*H* of N,S-Ph), 6.94 (2H, d, C*H* of pendant-Ph), 6.87 (1H, t, C*H* of N,S-Ph), 6.85 (1H, t, C*H* of N,S-Ph), 6.77 (1H, t, C*H* of N,S-Ph), 6.56 (1H, s, C*H*=N), 6.49 (1H, d, C*H* of N,S-Ph), 6.44 (1H, d, C*H* of N,S-Ph), 6.42 (2H, d, C*H* of pendant-Ph), 6.28 (1H, s, C*H*=N), 6.14 (1H, d, C*H* of N,S-Ph), 6.08 (1H, t, C*H* of N,S-Ph), 6.02 (1H, t, C*H* of N,S-Ph), 5.95 (2H, d, C*H* of pendant-Ph), 5.78 (1H, br, C*H* of N,S-Ph), 3.01 (6H, s, CH_3), 2.91 (6H, s, CH_3), 2.80 (6H, s, CH_3). Single crystals of **8** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a solution of **8** in $CHCl_3$.

(b) Synthesis of $[Cu_8(L^1)_8](PF_6)_2$ (9).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.39 mmol) in 5 mL of CH_3CN was added a solution containing of 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol) and Et_3N (0.04 g, 0.40 mmol) in 10 mL of $CHCl_3$. The mixture was stirred at room temperature for 5 min, which gave a dark red-brown solution. This reaction solution was concentrated to dryness, and the residue was dissolved in a mixture of $CHCl_3$ (5 mL) and MeOH (5 mL), followed by allowing it to stand at room temperature for one day in air. The resulting black crystals of **9** were collected by filtration. Yield: 0.11 g, 75%. Anal. Found: C, 47.63; H, 4.09; N, 7.36%. Calcd for $[Cu_8(L^1)_8](PF_6)_2\cdot2CHCl_3$: C, 47.58; H, 3.99; N, 7.28%. ^1H NMR (500 MHz, 1,2-dichloroethane-d_4, 0°C): δ 7.43 (1H, s, C*H*=N), 7.00 (1H, d, C*H* of N,S-Ph), 6.81 (1H, d, C*H* of N,S-Ph), 6.65-6.50 (3H, m, C*H* of N,S-Ph and C*H* of pendant-Ph), 6.42

(1H, d, *CH* of N,S-Ph), 3.17 (6H, s, CH_3). IR (KBr, cm^{-1}): 843 (PF_6^-), 558 (PF_6^-).

(c) Synthesis of $[Cu_3(L^2)_3]$ (10).

To a pale yellow solution of 2-(2,4,6-trimethylphenyl)benzothiazoline (0.26 g, 1.00 mmol) in 10 mL of $CHCl_3$ were sequentially added Et_3N (0.10 g, 1.01 mmol) and $[Cu(CH_3CN)_4]PF_6$ (0.37 g, 1.00 mmol) in 5 mL of CH_3CN. The reaction solution was stirred at room temperature for 30 min, concentrated to ca. 5 mL, and then 20 mL of EtOH was added to it. After the reaction mixture was stood in a freezer for 5 days, the resulting orange crystals of **10** were collected by filtration. Yield: 0.24 g, 69%. Anal. Found: C, 58.57; H, 5.11; N, 5.76%. Calcd for $[Cu_3(L^2)_3]\cdot1.3CH_3CN\cdot0.3CHCl_3$: C, 58.62; H, 5.04; N, 5.77%. ^{1}H NMR (400 MHz, $CDCl_3$, at 30°C): δ 8.47 (1H, s, *CH*=N), 7.00-6.80 (6H, m, *CH* of pendant-Ph and N,S-Ph), 2.33 (3H, s, CH_3) 2.27 (6H, s, CH_3). ^{1}H NMR (500 MHz, DMSO-d_6, at 30°C): δ 8.68 (1H, s, *CH*=N), 7.20 (1H, d, *CH* of N,S-Ph), 7.03 (1H, t, *CH* of N,S-Ph), 6.92 (1H, t, *CH* of N,S-Ph), 6.82 (2H, s, *CH* of pendant-Ph), 6.75 (1H, d, *CH* of N,S-Ph), 2.29 (3H, s, CH_3) 2.20 (6H, s, CH_3). Single crystals of **10** suitable for X-ray analysis were obtained by the recrystallization from CH_2Cl_2 and EtOH in a freezer.

(d) Synthesis of $[Cu_4(L^4)_4]$ (11).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.16 g, 0.43 mmol) in 5 mL of CH_3CN was added a mixture of 2-(9-anthracenyl)benzothiazoline (0.10 g, 0.32 mmol), Et_3N (0.03 g, 0.34 mmol), and Bu_4NBr (0.18 g, 0.55 mmol) in 50 mL of CH_3CN. The reaction mixture was stirred at room temperature for 5 min, followed by filtered to obtain a brown powder of **11**. Yield: 0.10 g, 66%. Anal. Found: C, 57.67; H, 3.22; N, 3.18%. Calcd for $[Cu_4(L^4)_4]\cdot2.5CHCl_3$: C, 57.65; H, 3.27; N, 3.11%. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 9.18 (1H, s, *CH*=N), 8.56 (1H, s, *CH* of pendant-Ar), 8.18 (2H, d, *CH* of pendant-Ar), 8.07 (2H, d, *CH* of pendant-Ar), 7.51 (2H, t, *CH* of pendant-Ar), 7.31 (2H, t, *CH* of pendant-Ar), 6.97 (1H, d, *CH* of N,S-Ph), 6.71 (1H, t, *CH* of N,S-Ph), 6.41 (1H, t, *CH* of N,S-Ph), 5.94 (1H, d, *CH* of N,S-Ph). ^{1}H NMR (400 MHz, DMSO-d_6, 30°C): δ 9.41 (1H, s, *CH*=N), 8.76 (1H, s, *CH* of pendant-Ar), 8.19 (2H, d, *CH* of pendant-Ar), 8.14 (2H, d, *CH* of pendant-Ar), 7.59 (2H, t, *CH* of pendant-Ar), 7.39 (2H, t, C*H* of pendant-Ar), 7.31 (1H, d, C*H* of N,S-Ph), 6.78 (1H, t, C*H* of N,S-Ph), 6.41 (1H, t, C*H* of N,S-Ph), 5.66 (1H, d, C*H* of N,S-Ph). Single crystals of **11** suitable for X-ray analysis were obtained by the slow diffusion of *n*-C_5H_{12} into a solution of **11** in $CHCl_3$.

(e) Synthesis of a mixture of $[Cu_8(L^1)_8](PF_6)_2$ (9) and $[Cu_{16}(L^1)_{12}Cl](PF_6)_3$ (12-Cl).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.39 mmol) in 5 mL of CH_3CN was added a solution containing 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol) and Et_3N (0.04 g, 0.40 mmol) in 10 mL of $CHCl_3$. The mixture was stirred at room temperature for 5 min, which gave a dark red-brown solution. A large amount of Et_2O (70 mL) was added to the reaction solution to precipitate a powder, which was then dissolved in $CHCl_3$ (20 mL). The solution was allowed to stand at room temperature for 4 days in air, which afforded a mixture (0.06 g) of black crystals **9** and red microcrystals of **12-Cl**. Single crystals of **12-Cl** suitable for X-ray analysis were obtained by dissolving the red microcrystals in MeOH, followed by allowing it to stand at room temperature for a week.

(f) Synthesis of $[Cu_{16}(L^1)_{12}Cl](PF_6)_3$ (12-Cl).

Method A: the 1:1 reaction of $[Cu(CH_3CN)_4]PF_6$ and 2-(4-dimethylaminophenyl)benzothiazoline.

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.15 g, 0.39 mmol) in 5 mL of CH_3CN was added a solution containing of 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol), Et_3N (0.04 g, 0.40 mmol) and Bu_4NCl (0.35 g, 1.26 mmol) in 10 mL of $CHCl_3$. The mixture was stirred at room temperature for 5 min, which gave a dark red solution. This reaction solution was concentrated to dryness, and the residue was dissolved in a mixture of CH_3CN (5 mL) and MeOH (10 mL). The addition of a large amount of Et_2O (150 mL) to the solution gave a red powder of **12-Cl**. Yield: 0.05 g, 40%. Anal. Found: C, 46.19; H, 4.14; N, 7.20%. Calcd for $[Cu_{16}(L^1)_{12}Cl](PF_6)_3 \cdot 7H_2O$: C, 46.22; H, 4.18; N, 7.19%. ^1H NMR (500 MHz, CD_3CN, 0°C): δ 9.50 (1H, d, C*H* of pendant-Ph), 7.89 (1H, s, C*H*=N), 7.22 (1H, d, C*H* of pendant-Ph), 7.03 (1H, d, C*H* of N,S-Ph), 6.85 (1H, d, C*H* of pendant-Ph), 6.52 (1H, d, C*H* of N,S-Ph), 6.47 (1H, t, C*H* of N,S-Ph), 6.19 (1H, d, C*H* of pendant-Ph), 6.14 (1H, t, C*H* of N,S-Ph), 2.67 (6H, s, CH_3).

Method B: the stoichiometric 4:3 reaction of $[Cu(CH_3CN)_4]PF_6$ and 2-(4-dimethylaminophenyl)benzothiazoline.

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.19 g, 0.52 mmol) in 5 mL of CH_3CN was added a suspension containing 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol), Et_3N (0.04 g, 0.40 mmol) and Bu_4NCl (0.19 g, 0.68 mmol) in 10 mL of MeOH. The mixture was stirred at room temperature for 5 min, and then filtered. The addition of a large amount of Et_2O (60 mL) to the resulting dark red filtrate quickly afforded a red powder of **12-Cl**, which was collected by filtration. Yield: 0.12 g, 76%.

(g) Synthesis of $[Cu_{16}(L^1)_{12}Br](PF_6)_3$ (12-Br).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.19 g, 0.52 mmol) in 5 mL of CH_3CN was added a suspension containing 2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol), Et_3N (0.04 g, 0.40 mmol) and Bu_4NBr (0.23 g, 0.71 mmol) in 10 mL of MeOH. The mixture was stirred at room temperature for 5 min, and then filtered. The addition of a large amount of Et_2O (60 mL) to the dark red solution quickly afforded a red powder of **12-Br**, which was collected by filtration. Yield: 0.12 g, 75%. Anal. Found: C, 45.47; H, 3.91; N, 7.03%. Calcd for $[Cu_{16}(L^1)_{12}Br](PF_6)_3 \cdot 8H_2O$: C, 45.62; H, 4.17; N, 7.09%. ^1H NMR (500 MHz, CD_3CN, 0°C): δ 9.49 (1H, d, C*H* of pendent-Ph), 7.89 (1H, s, C*H*=N), 7.21 (1H, d, C*H* of pendent-Ph), 7.01 (1H, d, C*H* of N,S-Ph), 6.85 (1H, d, C*H* of pendent-Ph), 6.53 (1H, d, C*H* of N,S-Ph), 6.48 (1H, t, C*H* of N,S-Ph), 6.18 (1H, d, C*H* of pendent-Ph), 6.15 (1H, t, C*H* of N,S-Ph), 2.67 (6H, s, CH_3). Single crystals of **12-Br** suitable for X-ray analysis were obtained by the crystallization of the red powder from MeOH containing Bu_4NBr and NH_4PF_6 in a freezer.

(h) Synthesis of $[Cu_{16}(L^1)_{12}I](PF_6)_3$ (12-I).

To a colorless solution of $[Cu(CH_3CN)_4]PF_6$ (0.19 g, 0.52 mmol) in 5 mL of deoxygenated CH_3CN was added a suspension containing

2-(4-dimethylaminophenyl)benzothiazoline (0.10 g, 0.39 mmol) and Et_3N (0.04 g, 0.40 mmol) in 10 mL of deoxygenated MeOH, followed by the addition of Bu_4NI (0.10 g, 0.26 mmol). The mixture was stirred at room temperature for 5 min under a nitrogen atmosphere and then filtered. The addition of a large amount of Et_2O (60 mL) to the dark red solution quickly afforded an orange-red powder of **12-I**, which was collected by filtration. Yield: 0.10 g, 67%. Anal. Found: C, 42.44; H, 3.64; N, 6.60%. Calcd for $[Cu_{16}(L^1)_{12}I](PF_6)_3 \cdot 2CuI \cdot 2H_2O$; C, 42.73; H, 3.67; N, 6.64%. ^{1}H NMR (500 MHz, CD_3CN, 0°C): δ 9.50 (1H, d, C*H* of pendent-Ph), 7.90 (1H, s, C*H*=N), 7.21 (1H, d, C*H* of pendent-Ph), 6.99 (1H, d, C*H* of N,S-Ph), 6.87 (1H, d, C*H* of pendent-Ph), 6.55-6.49 (2H, m, C*H* of N,S-Ph), 6.18-6.15 (2H, m, C*H* of pendent-Ph and C*H* of N,S-Ph), 2.67 (6H, s, CH_3). Single crystals of **12-I** suitable for X-ray analysis were obtained from the remaining filtrate when it was stored in a freezer.

II-3. Results and discussion.

II-3-1. Synthesis, structure, and characterization of Au^{I} complexes.

The 1:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with [AuCl(tht)] under the presence of Et_3N in $CHCl_3$ at room temperature gave a yellow solution, from which yellow powder of **1** was obtained in a high yield by adding n-C_6H_{14} as a poor solvent. Single crystals of **1** suitable for X-ray analysis were prepared by the slow diffusion of n-C_5H_{12} into the yellow reaction solution. A similar reaction using 2-(2,4,6-trimethylphenyl)benzothiazoline instead of 2-(4-dimethylaminophenyl)benzothiazoline gave yellow powder of **2** in a high yield. Single crystals of **2** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a solution of **2** in $CHCl_3$.

The elemental analytical data of **1** and **2** were in agreement with formulas containing Au atoms and iminothiophenolate ligands (L^1 or L^2) in a 1:1 ratio. These results suggest that **1** and **2** are neutral compounds. The ^{1}H NMR spectrum of **1** in $CDCl_3$ at 30°C is shown in Figure 2-1 (a). A singlet signal at around δ 8 ppm (1H; 8.04 ppm) was assigned to an azomethine proton of iminothiophenolate ligand L^1. It has been reported that the thiazoline proton signal of the starting benzothiazoline appears at δ 5-6 ppm as one singlet, while that of azomethine proton of iminothiophenolate appears at δ 7-9 ppm as one singlet.[16,17] Therefore, the ^{1}H NMR spectrum of **1** suggests that the iminothiophenolate-type ligand L^1 is formed and bind to Au^{I} ions in $CDCl_3$. Two doublet signals (2H; 7.67 and 6.49 ppm) were assigned to pendant-phenyl protons, suggestive of the free rotation of the substituent. The other two doublet (1H; 7.61 and 6.79 ppm) and two triplet signals (1H; 7.12 and 6.89 ppm) at an aromatic region were assigned to *N,S*-chelating phenyl protons. The ^{1}H NMR spectrum of **2** showed that the azomethine proton signal appears at a low magnetic field region (1H; 8.54 ppm) as found in **1** (Figure 2-1 (b)). In addition, one singlet signal assignable to the pendant phenyl proton and one singlet signal assignable to the *o*-methyl protons (6H; 2.49 ppm) were observed, suggestive of the free rotation of the substituent. The chemical shifts and patterns of other signals assignable to the *N,S*-chelating phenyl protons in L^2 were very similar to those of **1**. These results suggest that the structure of **2** is very similar to that of **1** in solution. ESI mass spectrum of **1** in CH_2Cl_2/MeOH (1:1) was dominated by a signal at m/z = 1809.3, the calculated mass and the isotopic distribution of which match well with those for tetranuclear complex $[Au_4(L^1)_4]+H^+$ (Figure 2-2). Considering these results and the preference of coordination mode of Au^I ion, it was found that **1** and **2** are S-bridged tetranuclear cyclic complexes with a high symmetrical $\{Au^I_4S_4\}$ core.

The structures of **1** and **2** were determined by single-crystal X-ray analysis. The crystallographic data of **1** and **2** are summarized in Table 2-1. The selected bond distances and angles of **1** and **2** are summarized in Tables 2-3 and 2-4. As shown in Figure 2-3, complex **1** is a tetranuclear cyclic Au^I_4 complex composed of four Au^I atoms and four iminothiophenolate ligands (L^1) as expected. The ligand L^1 is derived from the deprotonation of the 2-(4-dimethylaminophenyl)benzothiazoline, accompanied by the cleavage of a C–S bond. In **1**, four Au^I atoms are linked by four S atoms from four L^1 ligands to form an $\{Au^I_4S_4\}$ metalloring structure. Each Au^I atom has an almost linear geometry bound by two S atoms (av. S–Au–S = 177.07(8)°), while each S atom bridges two Au^I atoms with an angle close to 90° (av. Au–S–Au = 90.43(8)°). Furthermore, the four Au^I and the four S atoms lie almost on the same plane with nearly the same Au–S bond distances (av. Au–S = 2.311(2) Å). Thus, the shape of the $\{Au^I_4S_4\}$ metalloring in **1** is very close to a regular square having a molecular C_{2v} symmetry. Note that each L^1 ligand binds to Au^I ions only through its thiolate group to adopt a μ_2-κ^1S:κ^1S coordination mode and its imine group is not participated in the coordination with the averaged Au···N distance of 3.157(2) Å.

Complex **2** was a tetranuclear Au^I_4 cyclic complex reminiscent of **1** (Figure 2-4). Bond lengths and angles of **1** and **2** are similar each other except for one relatively short Au1···N1 distance (2.82 Å) due to the steric constraint of the methyl group in **2**.

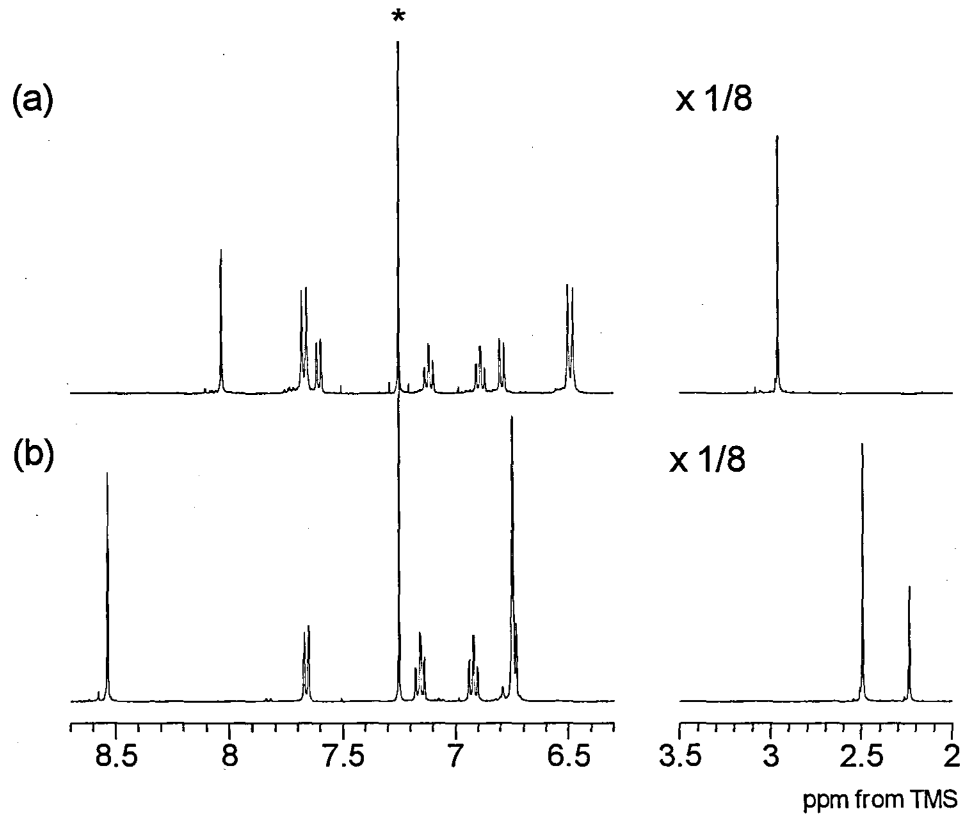


Figure 2-1. ^{1}H NMR spectra of (a) **1** and (b) **2** in $CDCl_3$ at 30°C. (*) denotes a signal of solvent.

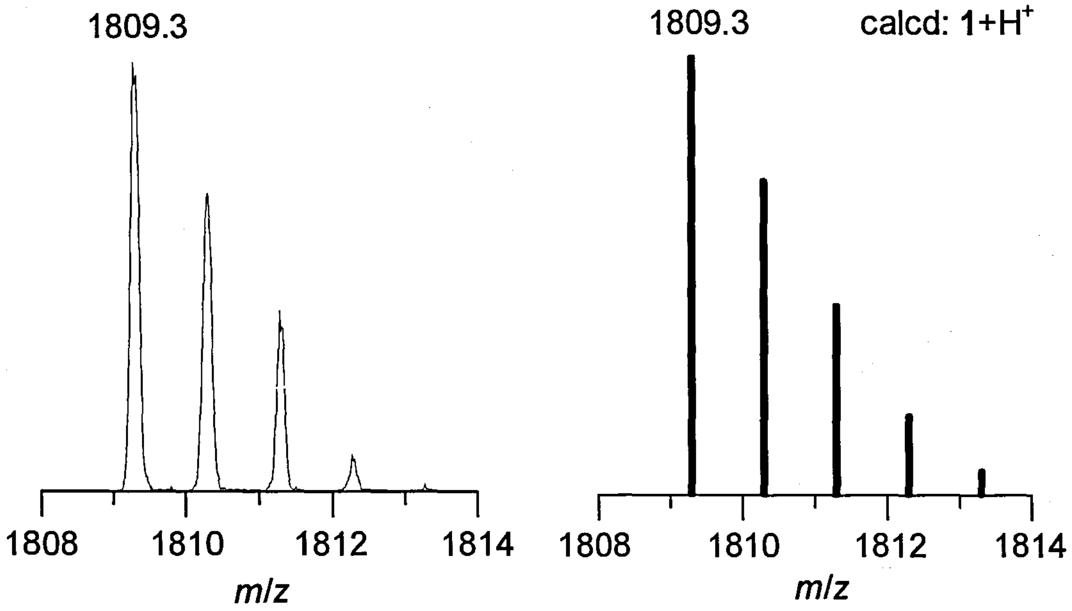


Figure 2-2. ESI mass spectrum of **1** in CH_2Cl_2/MeOH (1:1). Observed signal at *m*/*z* = 1809.3 (left) together with the calculated pattern for **1**+H^+ (right).

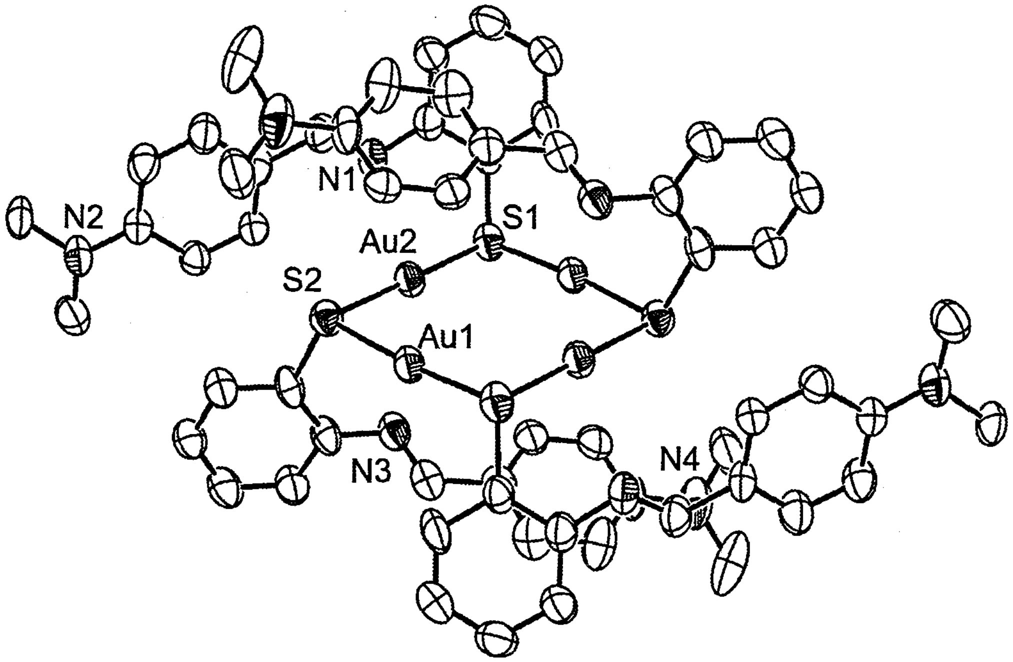


Figure 2-3. A perspective view of **1**. Hydrogen atoms are omitted for clarity.

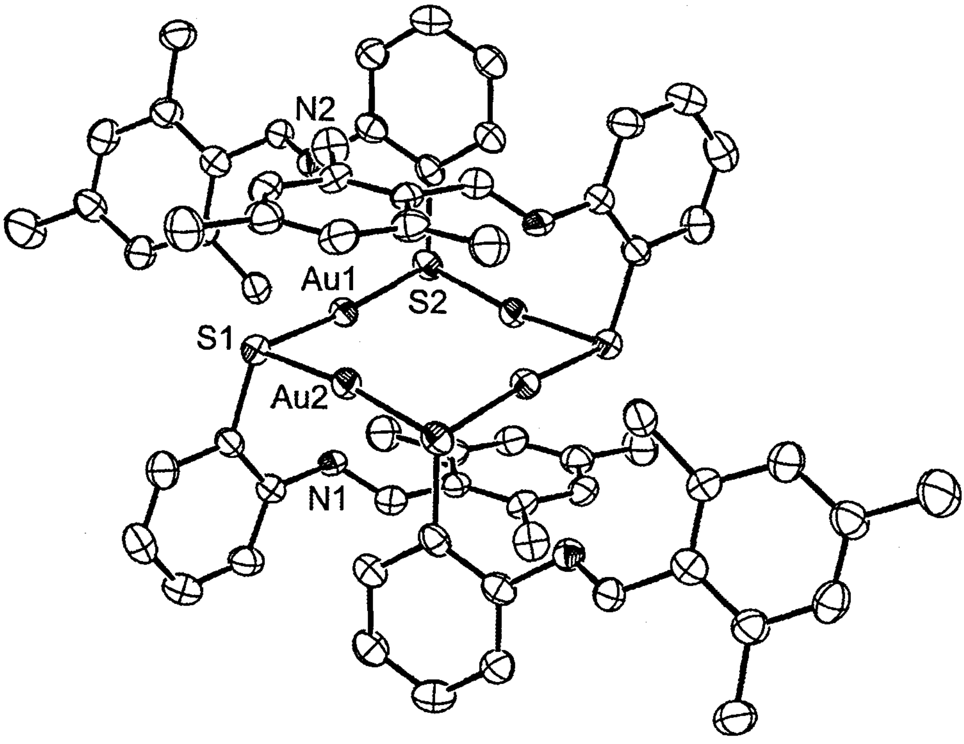


Figure 2-4. A perspective view of **2**. Hydrogen atoms are omitted for clarity.

II-3-2. Synthesis, structure, and characterization of Ag^I complexes.

The 1:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with silver(I) perchlorate under the presence of Et_3N in $CHCl_3$ at room temperature gave a yellow solution, from which yellow powder of **3** was obtained in a high yield. A similar reaction using silver(I) acetate instead of silver(I) perchlorate without the addition of Et_3N also gave complex **3**. When 2-(2,4,6-trimethylphenyl)benzothiazoline, 2-(1-naphtyl)benzothiazoline, 2-(9-anthracenyl)benzothiazoline, and 2-(4-methoxyphenyl)benzothiazoline were used instead of 2-(4-dimethylaminophenyl)benzothiazoline, yellow powders of **4**, **5**, **6**, and **7** were obtained, respectively. Single crystals of **3**, **5**, **6**, and **7** were prepared by the slow diffusion of n-C_5H_{12} into the reaction solutions. Single crystals of **4** were obtained by the slow diffusion of diethyl ether into a solution of **4** in $CHCl_3$.

The elemental analytical data of **3**–**7** were in agreement with formulas of tetranuclear Ag^I complexes $[Ag_4L_4]$ (L = L^1 (**3**), L^2 (**4**), L^3 (**5**), L^4 (**6**), L^5 (**7**)). These results suggest that complexes **3**–**7** are neutral compounds. While slightly broadened signals were observed in the ^1H NMR spectrum of **3** in $CDCl_3$ at 30°C (Figure 2-5 (a)), a single set of relatively sharp signals assignable to L^1 ligands appeared when it cooled to 0 °C (Figure 2-5 (b)). Only one singlet signal of azomethine proton was observed at 7.79 ppm. This result indicates that there is only one environment of ligand L^1 in complex **3**. In the ^1H NMR spectrum of **4**, one singlet signal of azomethine proton appeared at a lower magnetic field (1H; s, 8.47 ppm) similar to those of **1**–**3** (Figure 2-5 (c)), indicating that the ligand L^1 coordinates to the Ag^I ion (in an iminothiophenolate form), though the other signals overlapped one another and the assignments were difficult. Since complexes **5**–**7** were insoluble in any common organic solvents, the ^1H NMR spectra could not be measured for these samples. ESI mass spectrum of **3** in CH_2Cl_2/MeOH (1:1) showed a cluster of signals at m/z = 1560.9 for $[Ag_4(L^1)_4]+Ag^+$ instead of a signal at m/z = 1453 calculated for $[Ag_4(L^1)_4]+H^+$ (Figure 2-6). Considering that **3** is a tetranuclear metalloring similar to **1** (vide infra), this result shows that **3** is partially decomposed in solution, and it is consistent with the broadened signals in the ^1H NMR spectrum at 30°C.

The structures of **3-7** were determined by single-crystal X-ray analysis. The crystallographic data of **3-7** are summarized in Table 2-1. The selected bond distances and angles of **3-7** are summarized in Tables 2-5 to 2-9. As shown in Figure 2-7, **3** is a tetranuclear cyclic complex $[Ag_4(L^1)_4]$ composed of four Ag^I atoms and four iminothiolate ligands (L^1) as found in $[Au_4(L^1)_4]$ (**1**). However, in **3**, each L^1 ligand adopts a different coordination mode (μ_2-κ^1S:κ^2N,S) in contrast to the μ_2-κ^1S:κ^2S coordination mode in **1**. That is, an imine group in L^1 weakly coordinates to an Ag^I atom (av. Ag–N = 2.628(3) Å) and its thiolato group bridges two Ag^I atoms (av. Ag–S = 2.425(9) Å). As a result, two of four Ag^I atoms were situated in a distorted tetrahedral geometry coordinated by two imine N and two thiolato S atoms, whereas the others are in a digonal geometry coordinated by two thiolato S atoms (2,4-coordination manner; Chart 2 (a)). The difference in the coordination mode seriously influenced to the S–Ag–S angles (145.37(3)° for two tetrahedral Ag^I ions, 166.84(3)° for two digonal Ag^I ions). In addition, the four Ag–S–Ag angles are considerably deviated from 90° with the two angles being acute (Ag–S–Ag = 76.59(3)°) and the others being obtuse (Ag–S–Ag = 102.13(3)°). Thus, the metalloring structure having a molecular C_i symmetry in **3** is distorted from a regular square. This is attributed to the larger flexibility of coordination geometry of Ag^I compared with that of Au^I, as well as the larger affinity of an imine group to an Ag^I center compared with that to an Au^I center.

X-ray analysis demonstrated that complex **4** is also a tetranuclear cyclic complex composed of four Ag^I atoms and four iminothiophenolate ligands (L^2), which adopts a μ_2-κ^1S:κ^2N,S coordination mode, as found in the structure of **3** (Figure 2-8). However, four imine groups from four L^2 ligands bind to four different Ag^I atoms in **4**, and thus, all Ag^I atoms are situated in a T-shaped geometry coordinated by two thiolato S and a imino N atoms (3,3-coordination manner; Chart 2 (b)), unlike the S_2 digonal and N_2S_2 tetrahedral Ag^I atoms found in **3**. In **4**, each imine groups of L^2 ligand weakly coordinates to an Ag^I atom (av. Ag–N = 2.574(6) Å) and its thiolato group bridges two Ag^I atoms by nearly linear S–Au–S angles (av. Ag–S = 2.398(2) Å, av. S–Ag–S = 165.41(5)°). In addition, the four Ag–S–Ag angles are deviated from 90° with the two angles being acute (Ag–S–Ag = 80.79(5)°) and the others being obtuse (Ag–S–Ag = 97.20(6)°). Thus, the metalloring structure having a molecular C_i symmetry in **4** is distorted from a regular square.

As shown in Figures 2-9 and 2-10, complexes **5** and **6** have a tetranuclear cyclic structure with a 2,4-coordination manner, in which Ag^I ions adopt N_2S_2 distorted tetrahedral and S_2 digonal geometries. This structural feature is the same as that in **3**. There exist two sets of intramolecular π-π interaction (3.63(2) Å) between *N*,*S*-chelating phenyl rings and pendent anthracenyl group in **6**. The metalloring of complex **7** is reminiscent of that of **4**, where all Ag^I ions adopt an NS_2 T-shaped geometry (3,3-coordination manner) (Figure 2-11).

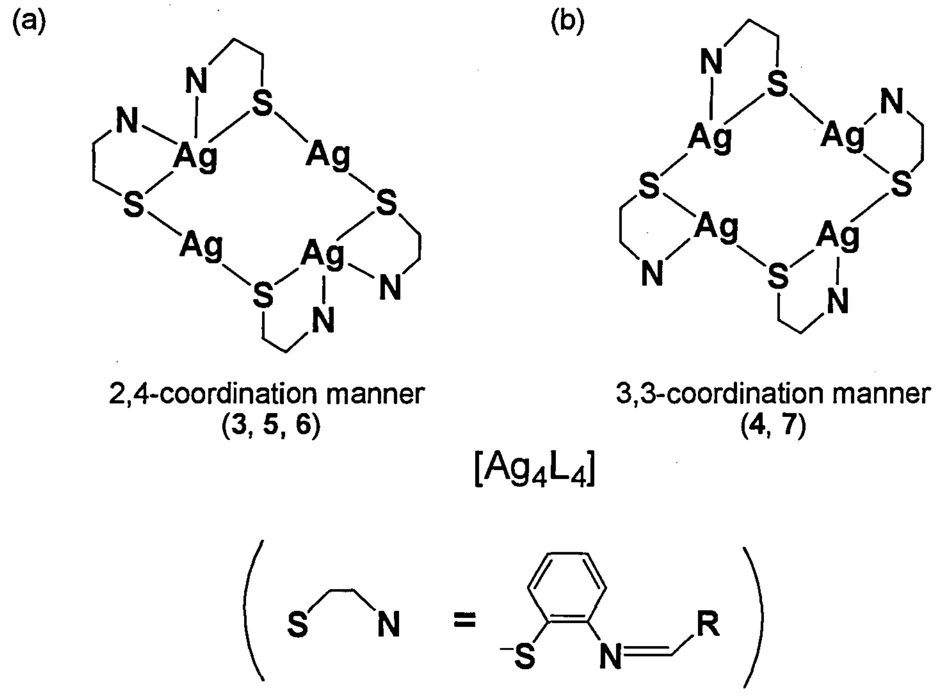


Chart 2. $\{Ag^{I}_{4}S_{4}\}$ rings with (a) 2,4-coordination manner for **3**, **5**, and **7** and (b) 3,3-coordination manner for **4** and 7.

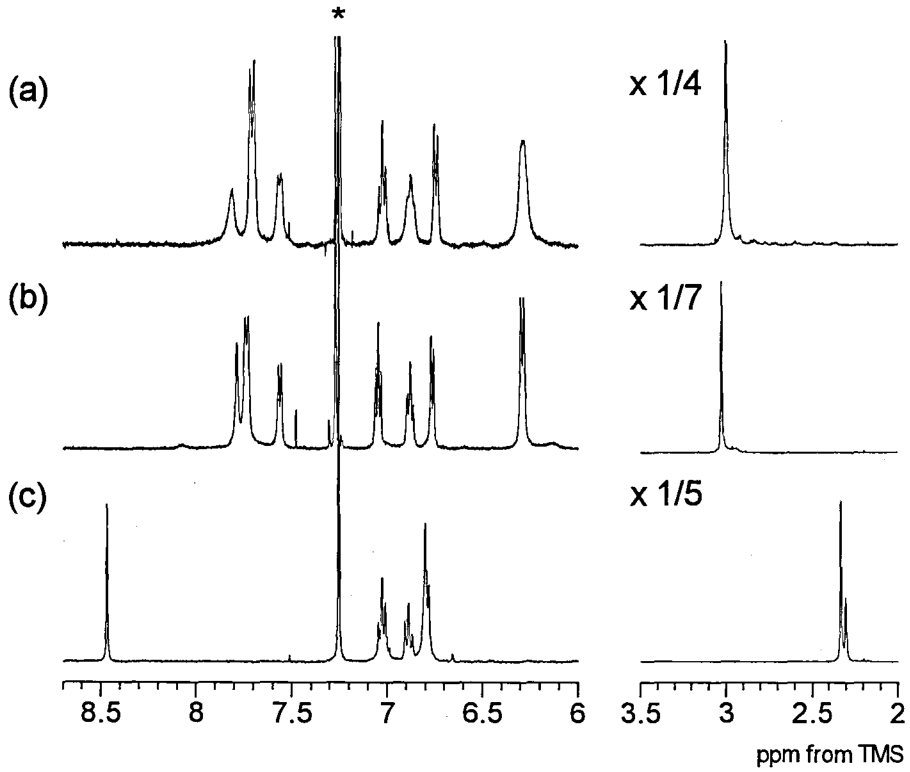


Figure 2-5. ^{1}H NMR spectra of (a) **3** at 30°C, (b) **3** at 0°C, and (c) **4** at 30°C in $CDCl_3$. (*) denotes a signal of solvent.

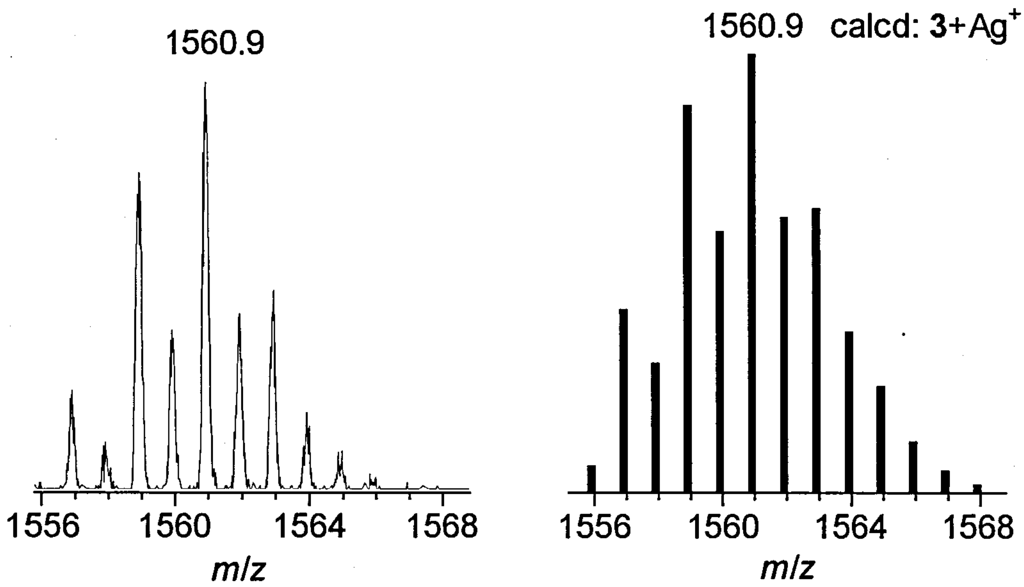


Figure 2-6. ESI mass spectrum of **3** in CH_2Cl_2/MeOH (1:1). Observed signal at *m*/*z* = 1560.9 (left) together with the calculated pattern for **3**+Ag^+ (right).

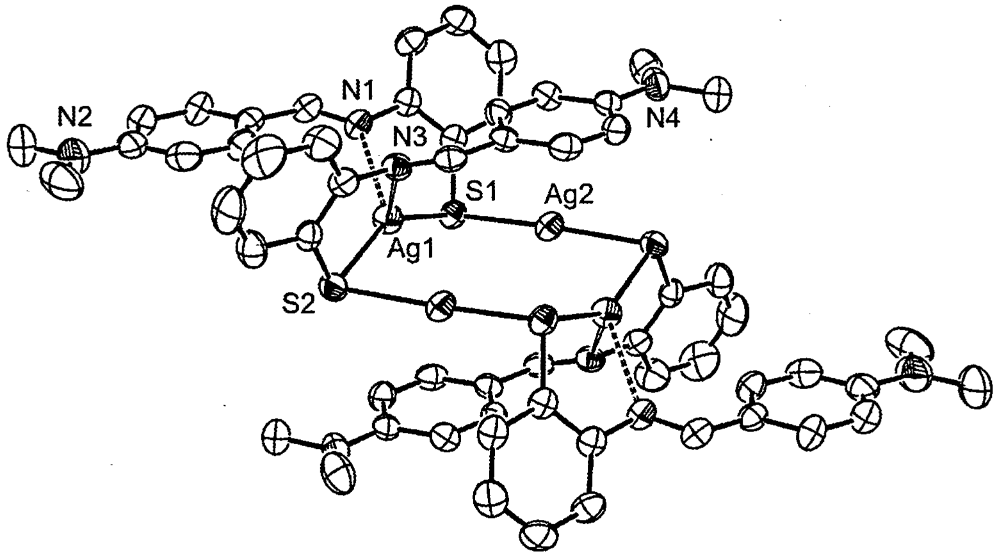


Figure 2-7. A perspective view of **3**. Hydrogen atoms are omitted for clarity.

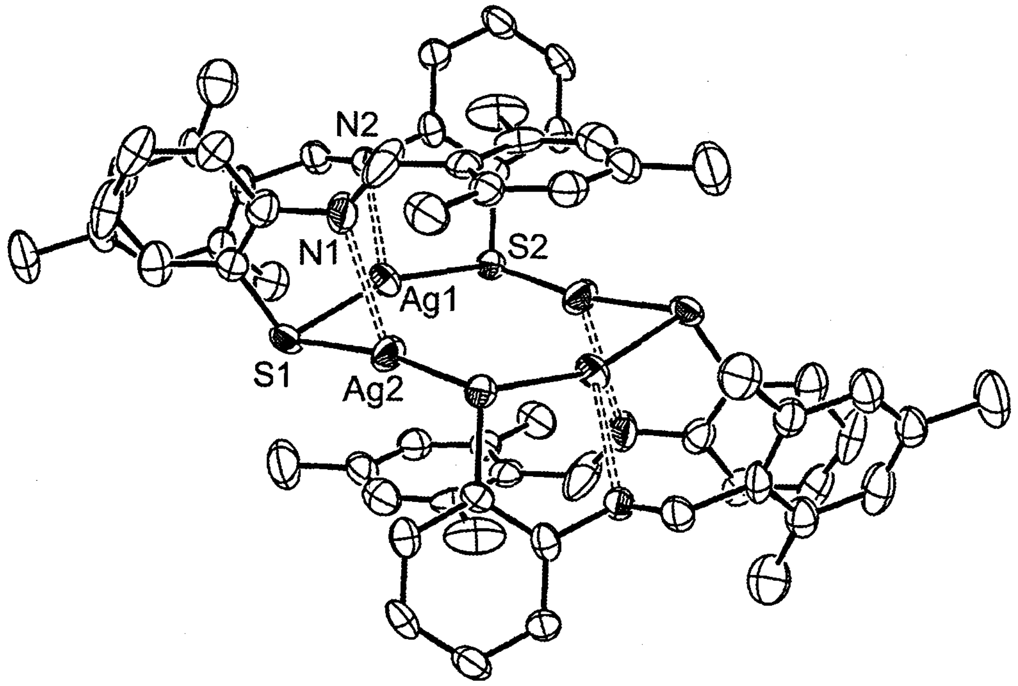


Figure 2-8. A perspective view of **4**. Hydrogen atoms are omitted for clarity.

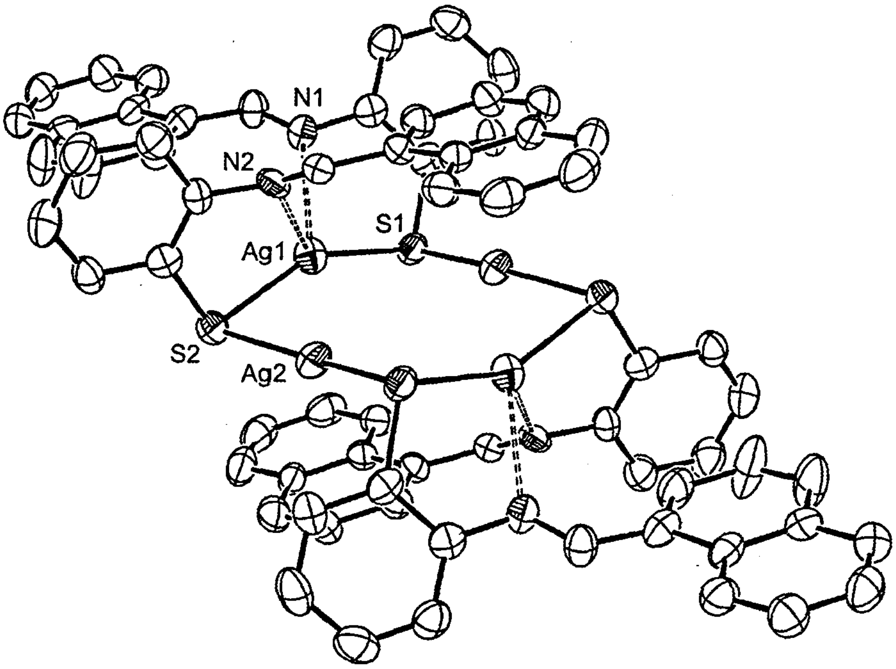


Figure 2-9. A perspective view of **5**. Hydrogen atoms are omitted for clarity.

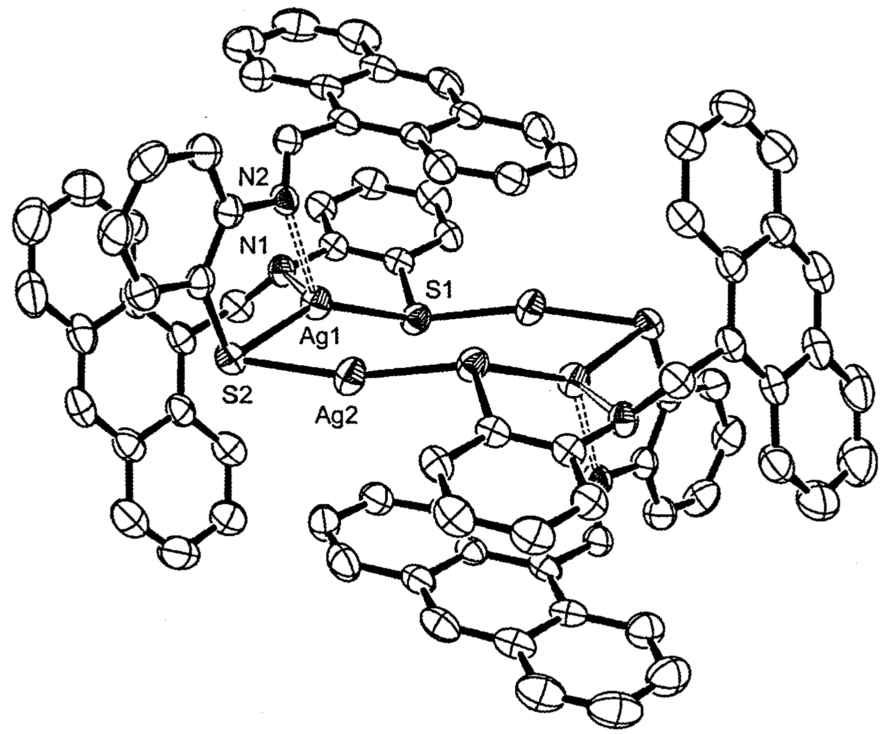


Figure 2-10. A perspective view of **6**. Hydrogen atoms are omitted for clarity.

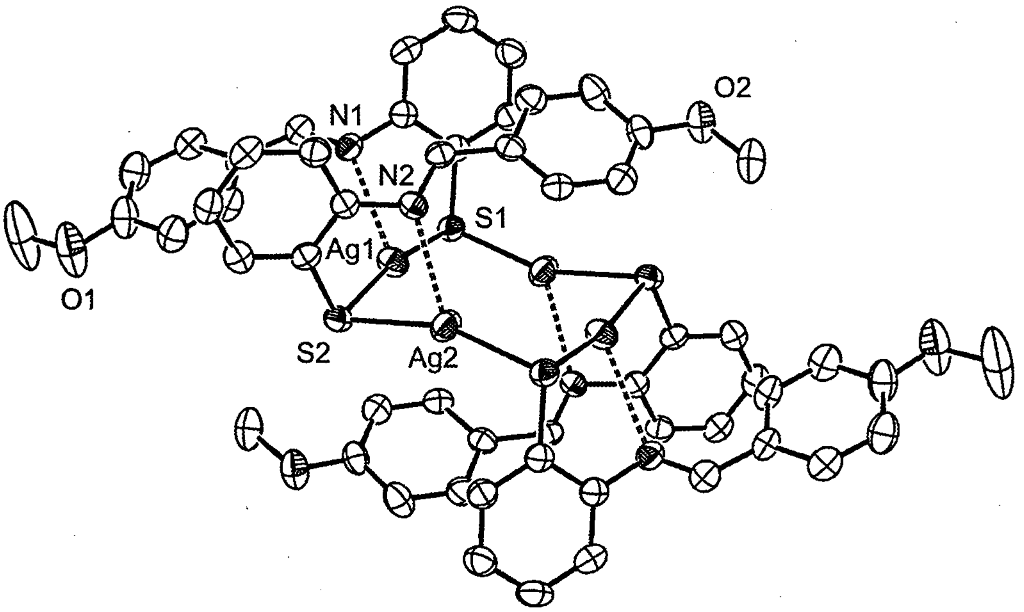


Figure 2-11. A perspective view of **7**. Hydrogen atoms are omitted for clarity.

II-3-3. Synthesis, structure, and characterization of Cu^I complexes.

The reaction of [Cu(CH_3CN)$_4$]PF_6 with an equimolar amount of deprotonated 2-(4-dimethylaminophenyl)benzothiazoline in CH_3CN/MeOH immediately gave a red powder of **8** quantitatively. A similar reaction in CH_3CN/$CHCl_3$ instead of CH_3CN/MeOH gave black crystals of **9** in a satisfactory yield. The 1:1 reaction of [Cu(CH_3CN)$_4$]PF_6 with deprotonated 2-(2,4,6-trimethylphenyl)benzothiazoline in CH_3CN/$CHCl_3$ gave orange crystals of **10** in a good yield. The 4:3 reaction of [Cu(CH_3CN)$_4$]PF_6 with deprotonated 2-(9-anthracenyl)benzothiazoline in CH_3CN under the presence of a small excess amount of Bu_4NBr gave a brown powder of **11** in a moderate yield.

The IR spectrum of **8** showed intense absorption bands at 843 and 558 cm^{-1} corresponding to the PF_6^- anion, which suggests that **8** is a cationic compound. The ^{1}H NMR spectrum of **8** in CD_3CN showed three sets of signals for L^1 ligands which were clearly confirmed by six singlet signals including three azomethine proton signals (δ 8.49, 6.56, and 6.28 ppm) and three methyl proton signals (δ 3.01, 2.91, and 2.80 ppm) (Figure 2-12 (a)). This result indicates that there are three different environments of ligand L^1 in complex **8**. The sharp signals imply that the copper ions in complex **8** are the +1 oxidation state and **8** are a diamagnetic copper(I) complex. The elemental analytical data of **8** were in agreement with a formula containing Cu atoms, iminothiolate ligands L^1, and PF_6^- anion in a 10:9:1 ratio. The diffuse reflection spectrum of **8** showed no near-infrared band, suggestive of the absence of the monovalent and divalent octanuclear copper clusters, $[Cu_8(L^1)_8]^+$ and $[Cu_8(L^1)_8]^{2+}$ (Figure 2-13).[17] Compound **9** was confidently assigned as a PF_6^- salt of the divalent octanuclear cluster, $[Cu_8(L^1)_8]^{2+}$, based on its IR spectrum and absorption spectrum that exhibits a characteristic intense near-infrared band at 1223 nm (Figure 2-14), besides its ^{1}H NMR spectrum (Figure 2-12 (b)) and elemental analysis.[17] The elemental analytical data of **10** and **11** were in agreement with formulas containing Cu atoms and iminothiolate ligands (L^2 or L^4) in a 1:1 ratio. The absence of PF_6^- anion in the IR spectra of **10** and **11** indicated that these complexes are not cationic unlike **8** and **9**. In addition, in the ^{1}H NMR spectra of **10** and **11**, a single set of signals for four L^2 or L^4 ligands was observed (Figures 2-12 (c) and (d)). These results indicate that the C_3 and

C_i symmetrical structures of $[Cu_3(L^2)_3]$ and $[Cu_4(L^4)_4]$ are retained in solution, of which solid state structures were determined by X-ray analysis for **10** and **11**, respectively (*vide infra*).

The molecular structures of **8, 10,** and **11** were successfully determined by single-crystal X-ray analysis. The crystallographic data are summarized in Table 2-2. The selected bond distances and angles are summarized in Tables 2-10 to 2-12.

Single crystals of **8** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a solution of **8** in $CHCl_3$. As shown in Figure 2-15, **8** is an S-bridged decanuclear cluster composed of ten Cu^I atoms and nine iminothiophenolate ligands L^1, which is sharp contrast to the tetranuclear Au^I_4 or Ag^I_4 metallorings. The asymmetric unit of crystal **8** contains one decacopper cluster cation, $[Cu_{10}(L^1)_9]^+$. Due to the poor crystal quality, the PF_6^- anion could not be modeled in the structure of **8**. The decacopper cluster cation comprises two kinds of units. One is an almost planar heptacopper unit, $\{Cu^I_7(L^1)_6\}^+$, and the other is a tricopper metalloring, $\{Cu^I_3(L^1)_3\}$. In the heptacopper $\{Cu^I_7(L^1)_6\}^+$ unit, three tetrahedral $\{Cu^I(L^1\text{-}N,S)_2\}^-$ units were spanned by three Cu^I ions through S atoms of L^1 ligands, forming a cyclic $\{Cu^I_6(L^1)_6\}$ unit (av. Cu–S = 2.283(8) Å, av. Cu–N = 2.138(19) Å). In addition, a Cu^I ion is accommodated in the center of the cyclic $\{Cu^I_6(L^1)_6\}$ unit through three S atoms of L^1 ligand (av. Cu–S = 2.281(8) Å) to give the monocationic heptacopper unit $\{Cu^I_7(L^1)_6\}^+$. On the other hand, the tricopper metalloring $\{Cu^I_3(L^1)_3\}$ is composed of three $\{Cu^I(L^1\text{-}N,S)\}$ units that are self-assembled through a Cu–S bond formation (av. Cu–S = 2.258(8) Å, av. Cu–N = 2.067(19) Å). Finally, each of three sulfur atoms of the $\{Cu^I_3(L^1)_3\}$ metalloring coordinate to three bridging Cu^I centers in $\{Cu^I_7(L^1)_6\}^+$ to complete the decacopper cluster cation, $[Cu_{10}(L^1)_9]^+$ (av. Cu–S = 2.231(8) Å). There is one pseudo C_3 axis in $[Cu_{10}(L^1)_9]^+$, thus, it is expected that there are three kinds of L^1 ligands in $[Cu_{10}(L^1)_9]^+$ in solution. In fact, three sets of signals of L^1 ligands were observed in the ^1H NMR spectra of **8** (*vide supra*). In $[Cu_{10}(L^1)_9]^+$, two kinds of coordination modes (μ_3-κ^1S:κ^1S:κ^2N,S and μ_2-κ^1S:κ^2N,S) and three kinds of coordination environments (trigonal-planer S_3, trigonal-planer NS_2, and tetrahedral N_2S_2) are observed for L^1 ligands and Cu^I ions, respectively.

Single crystals of **10** suitable for X-ray analysis were obtained by the recrystallization of **10** from CH_2Cl_2 and EtOH in a freezer. As shown in Figure 2-16, **10** is a trinuclear cyclic complex composed of three Cu^I atoms and three iminothiolate ligands L^2, which is reminiscent of the $\{Cu^I_3(L^1)_3\}$ unit found in **8**. In **10**, each of L^2 adopts a μ_2-κ^1S:κ^2N,S coordination mode, and three imino groups of L^2 ligands bind to three different Cu^I atoms to avoid a steric repulsion between bulky 2,4,6-trimethylphenyl groups. As a result, all Cu^I atoms are situated in an NS_2 T-shaped geometry (S–Cu–S = 165.41(5)°).

Single crystals of **11** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a solution of **11** in $CHCl_3$. As shown in Figure 2-17, **11** is a tetranuclear cyclic complex composed of four Cu^I ions and four iminothiophenolate ligands L^4. The overall structure of **11** is reminiscent of that of $[Ag_4(L^4)_4]$ (**6**). In **11**, each L^4 ligand adopts a μ_2-κ^1S:κ^2N,S coordination mode. Two of four Cu^I ions are situated in a distorted tetrahedral geometry coordinated by two imine N and two thiolato S atoms, whereas the others are in a digonal geometry coordinated by two thiolato S atoms and the tetranuclear ring structure with a 2,4-coordination manner is formed. In **11**, there exist two intramolecular π-π interactions (3.5 Å) between *N,S*-chelating phenyl rings and pendent anthracenyl rings.

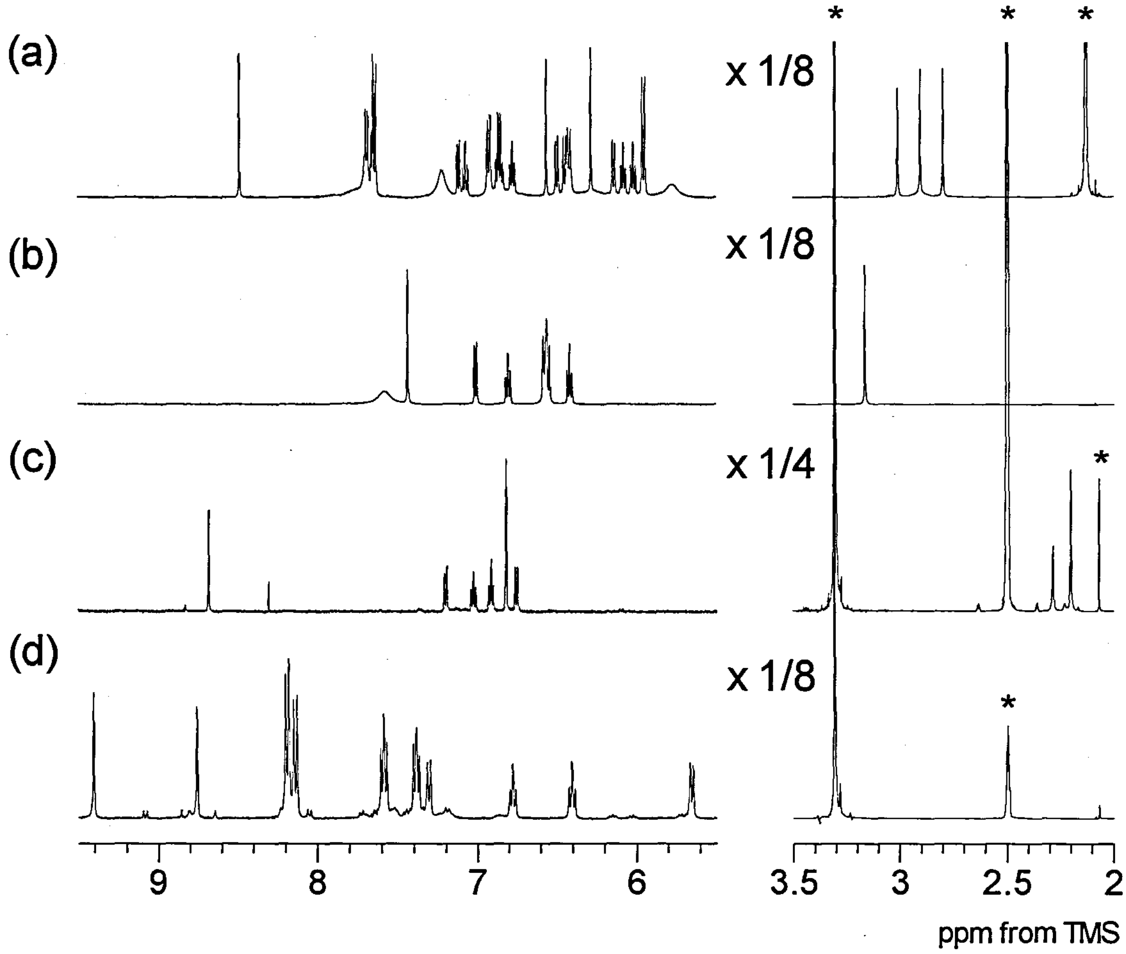


Figure 2-12. ^{1}H NMR spectra of (a) **8** in CD_3CN, (b) **9** in 1,2-dichloroethane-d_4, (c) **10** in DMSO-d_6, and (d) **11** in DMSO-d_6, at 30°C. (*) denotes a signal of solvent.

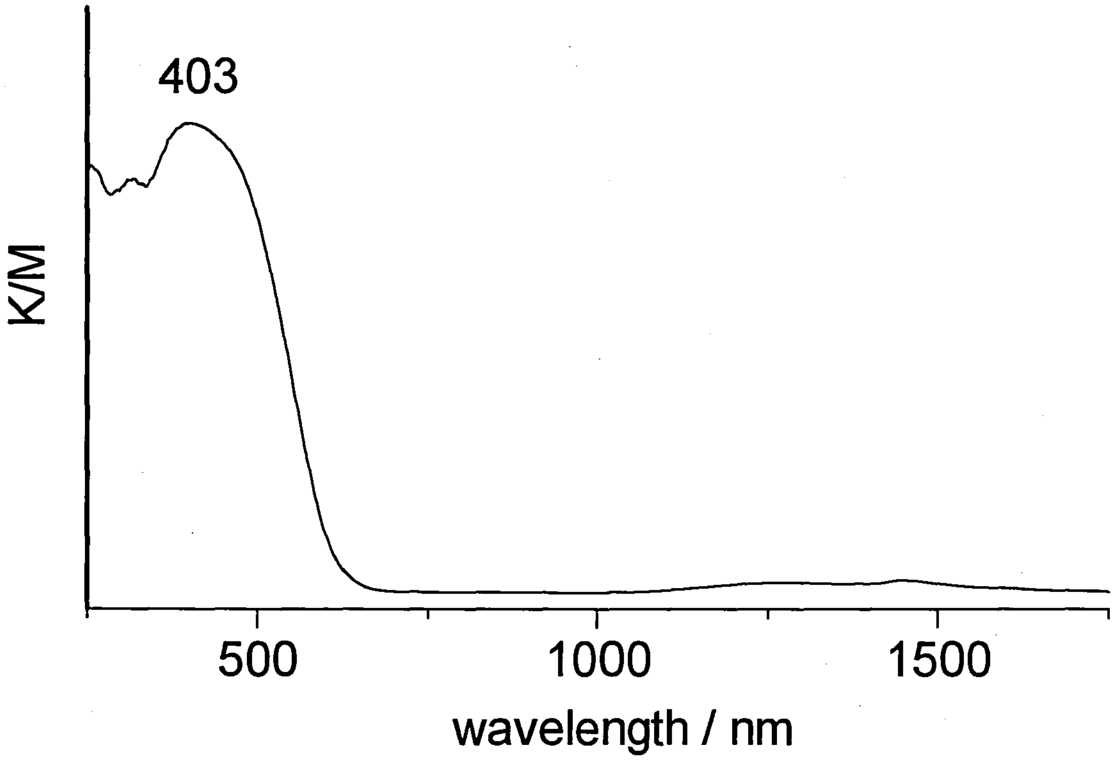


Figure 2-13. Diffuse reflection spectrum of **8**.

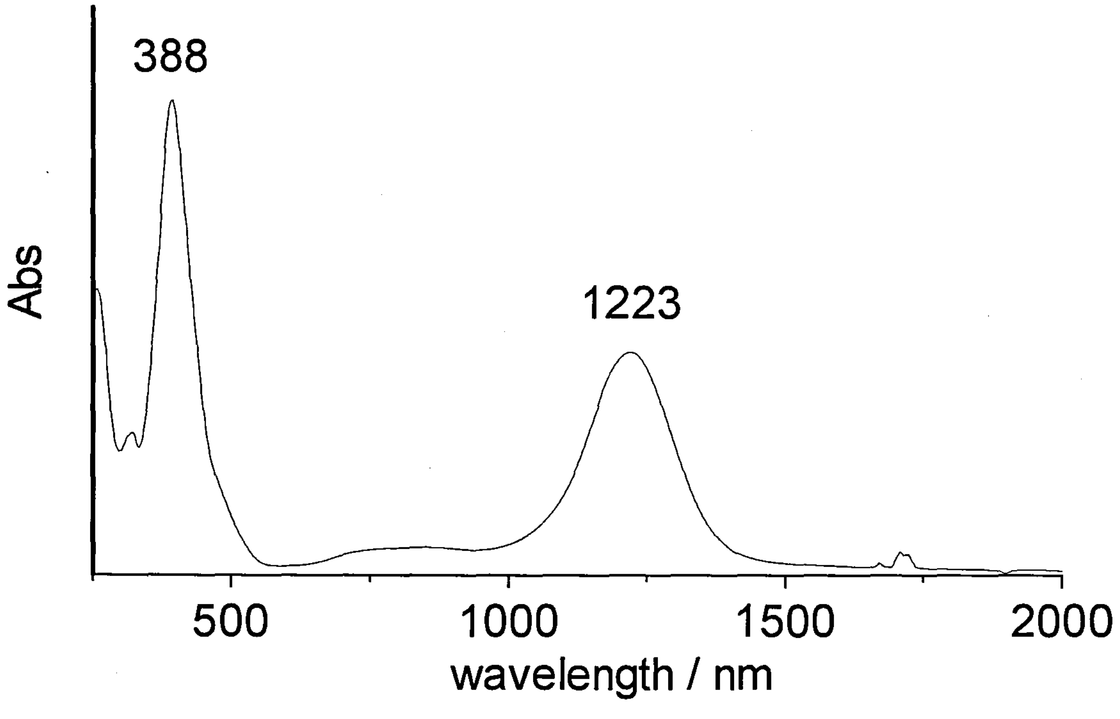


Figure 2-14. Absorption spectrum of **9** in 1,2-dichloroethane.

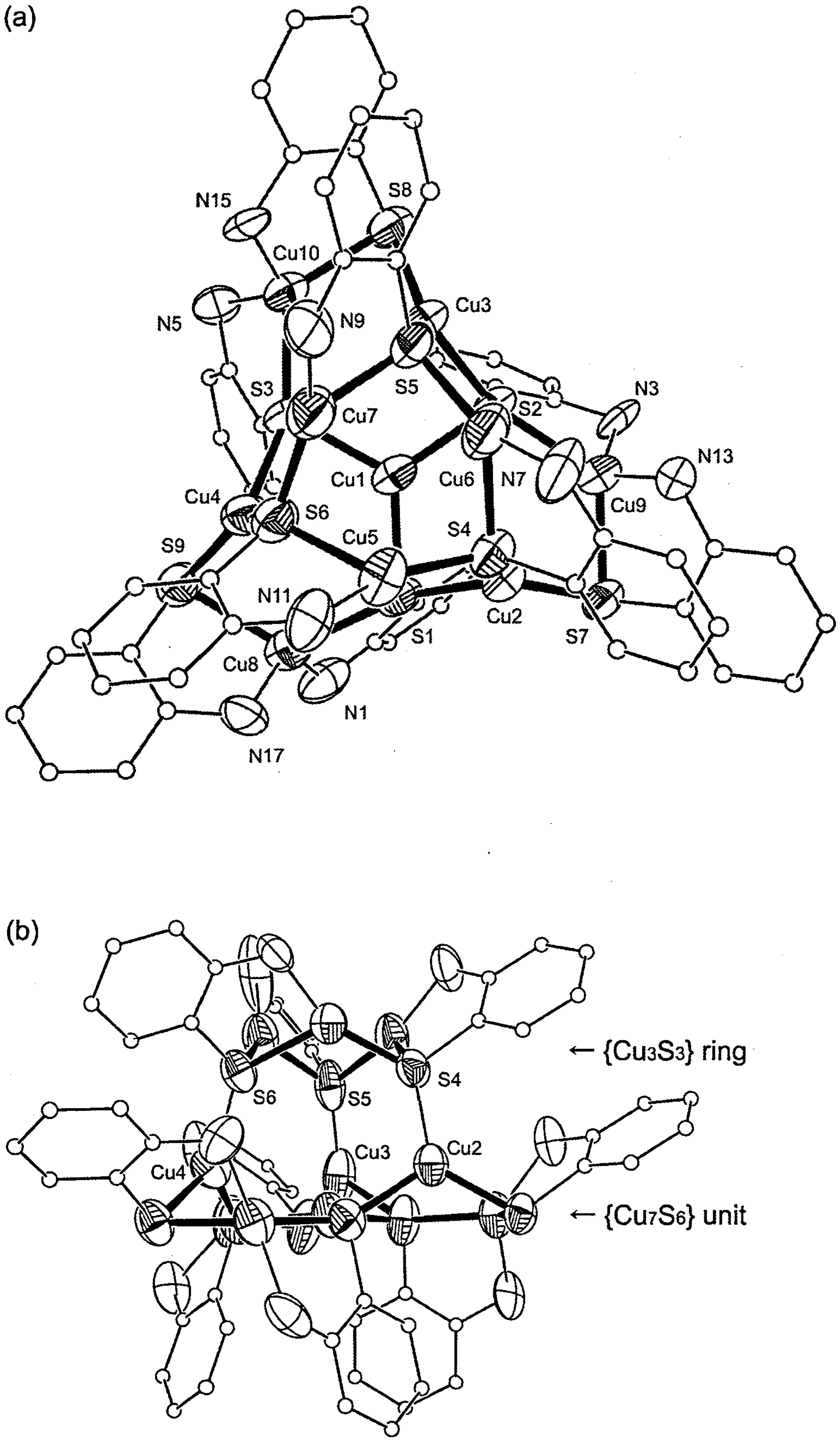


Figure 2-15. Perspective views of **8**. (a) Top view and (b) side view. Hydrogen atoms, imino-C, and pendant groups of L^1 are omitted for clarity.

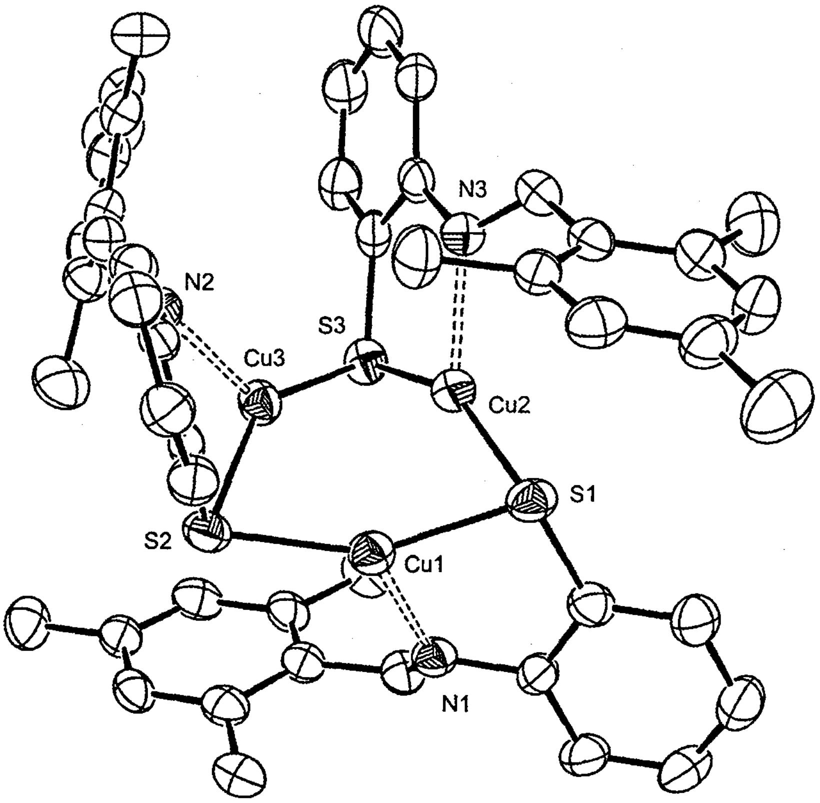


Figure 2-16. A perspective view of **10**. Hydrogen atoms are omitted for clarity.

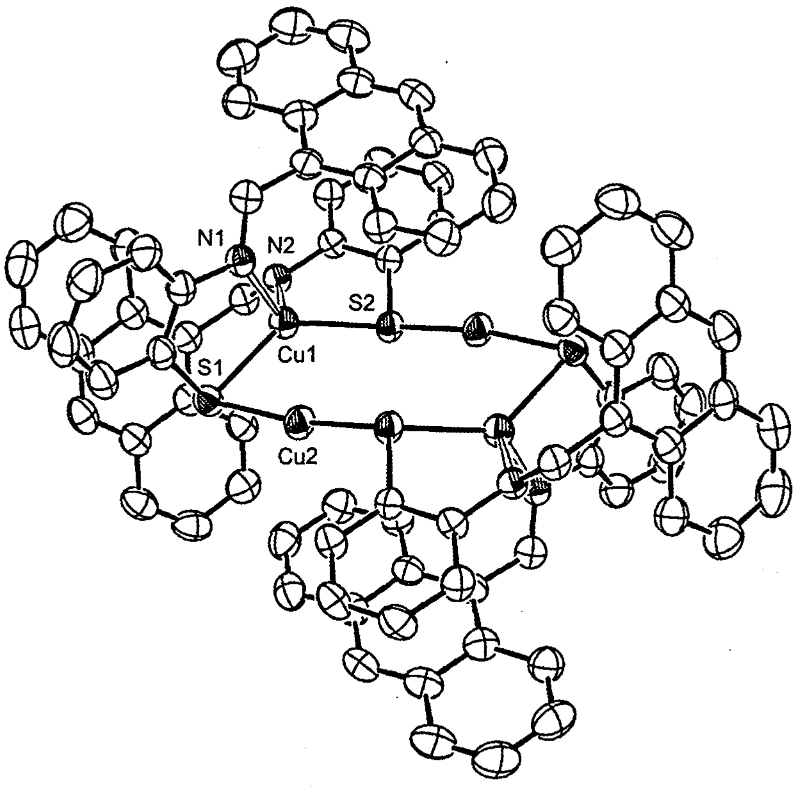


Figure 2-17. A perspective view of **11**. Hydrogen atoms are omitted for clarity.

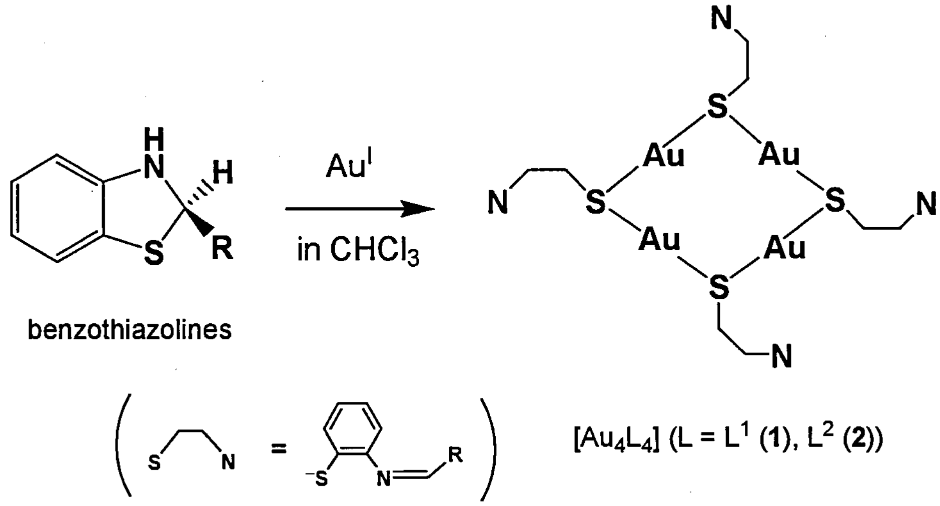
II-3-4. Substituent effect on multinuclear structures.

It was found that the reactions of benzothiazolines with [AuCl(tht)] afforded the tetranuclear metallorings $[Au_4L_4]$ ($L = L^1$ (**1**), L^2 (**2**)) with an S-bridged cyclic core $\{Au^I{}_4S_4\}$, in which each of L^1 and L^2 ligand bound to two Au^I ions only through its thiolate group (Scheme 2-1). In these structures, L^1 and L^2 commonly adopted a μ_2-κ^1S:κ^1S coordination mode and none of imine groups contacted to the Au^I centers. The bond lengths (av. Au–S = 2.311(2) Å for **1**, 2.307(2) Å for **2**) and angles (av. S–Au–S = 177.07(8)° for **1**, 172.55(6)° for **2**; Au–S–Au = 90.43(8)° for **1**, 88.86(5)° for **2**) are very similar to each other. Therefore, we concluded that no substituent effect was observed in Au^I system. It is assumed that the lack of Au–N coordination bonds in this system allow the pendant phenyl groups to separate each other, which cancels the substituent effect.

For Ag^I complexes, the reactions of benzothiazolines with Ag^I ion led to the tetranuclear metallorings $[Ag_4L_4]$ ($L = L^1$ (**3**), L^2 (**4**), L^3 (**5**), L^4 (**6**), L^5 (**7**)) with an S-bridged cyclic core $\{Ag^I{}_4S_4\}$ as found in the Au^I complexes (Scheme 2-2). This is probably because Ag^I ions also tend to adopt a linear-type coordination geometry. However, because of the flexible coordination environment of Ag^I ions, imine groups can coordinate to the Ag^I center in the Ag^I complexes in sharp contrast to the Au^I complexes. As the result, two types of metallorings with a different coordination environment around Ag^I ion were observed. One is 2,4-coordination manner, in which Ag^I atoms are situated in a S_2 diagonal, and N_2S_2 distorted tetrahedral geometries and the other is 3,3-coordination manner, in which all Ag^I atoms are situated in an NS_2 T-shaped geometry (Scheme 2-2). Three of five ligands (L^1, L^3, and L^4) formed the former type $Ag^I{}_4$ structure, while two ligands (L^2 and L^5) formed the latter type structure. The presence of two types of coordination manner is indicative of the flexible coordination behavior of Ag^I ions, as well as the existence of some substituent effect in the Ag^I system. However, obvious tendency of the substituent effect was not observed. It should be noted that a similar $\{Ag^I{}_4S_4\}$ ring which has two types of coordination manners in a crystal structure at the same time has been reported.[18]

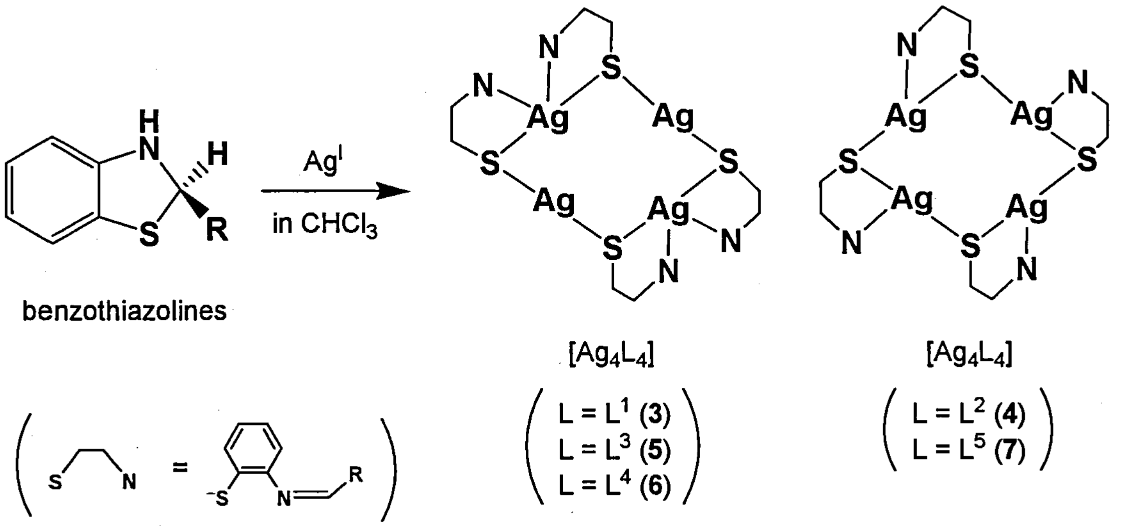
For Cu^I complexes, the reactions of benzothiazolines with Cu^I ion gave the S-bridged structures with various nuclearities, $[Cu_{10}(L^1)_9]PF_6$ (**8**), $[Cu_8(L^1)_8](PF_6)_2$ (**9**), $[Cu_3(L^2)_3]$

(**10**), $[Cu_4(L^4)_4]$ (**11**) (Scheme 2-3). As found in the Ag^I complexes, all imine groups coordinate to Cu^I ions in **8**, **9**, **10**, and **11**. However, not only μ_2 but also μ_3 thiolato-bridged structures were found in Cu^I system, leading to the formation of large clusters with higher nuclearity. Compared to the Au^I and Ag^I systems, relatively large substituent effect was observed in the Cu^I system. When 2-(4-dimethylaminophenyl)benzothiazoline that has a relatively small substituent group was employed as a ligand, large clusters with a higher nuclearity (**8** and **9**) were formed by using CH_3CN/MeOH or $CH_3CN/CHCl_3$ solvent, respectively. On the other hand, the use of benzothiazolines that have a bulky substituent group, such as 2-(2,4,6-trimethylphenyl)benzothiazoline and 2-(9-anthracenyl)benzothiazoline, gave small $\{Cu^I{}_nS_n\}$ metallorings (n = 3 and 4) with a lower nuclearity (**10** and **11**). In the large clusters with a higher nuclearity, the ligands get close to each other, and thus, the formation of these clusters may be prevented by the presence of bulky ligands due to the steric constraint of the substituent groups.[19] The difference in the nuclearity between **10** and **11** may come from the nature of the substituent groups. In **11**, the π-π interactions between *N*,*S*-chelating phenyl rings and anthracenyl groups are formed, which may stabilize the tetranuclear structure of **11**. On the other hand, the presence of methyl groups in L^2 prevent such a π-π interactions, which may lead to the formation of trinuclear structure of **10**.



$[Au_4L_4]$ (L = L^1 (**1**), L^2 (**2**))

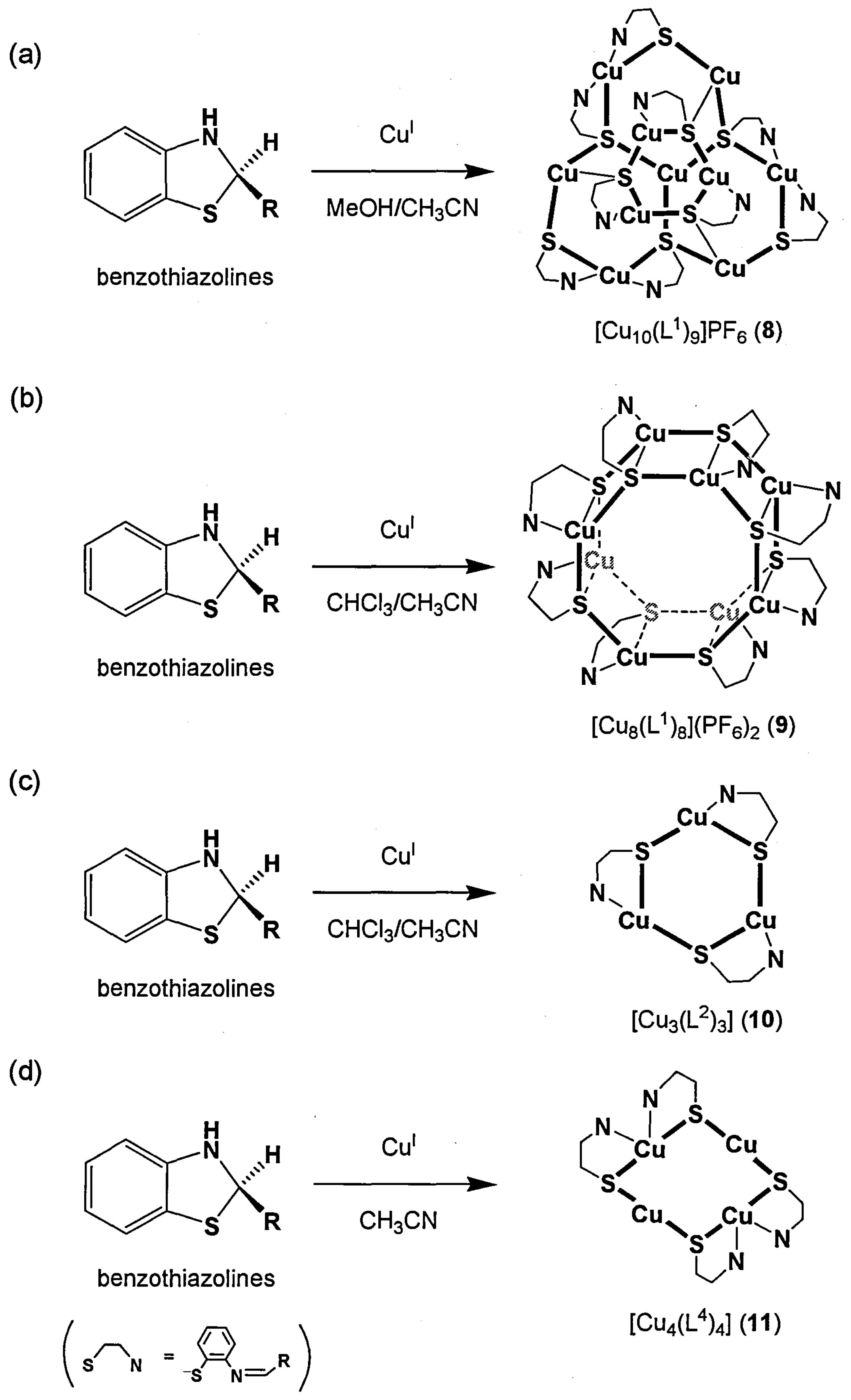
Scheme 2-1. Reactions of benzothiazolines with Au^I ion.



$[Ag_4L_4]$
L = L^1 (**3**)
L = L^3 (**5**)
L = L^4 (**6**)
2,4-coordination manner

$[Ag_4L_4]$
L = L^2 (**4**)
L = L^5 (**7**)
3,3-coordination manner

Scheme 2-2. Reactions of benzothiazolines with Ag^I ion.



Scheme 2-3. Reactions of benzothiazolines with Cu^I ion.

II-3-5. Template effect of halide ions on Cu^I complexes.

II-3-5-1. Synthesis, structure, and characterization of $[Cu_{16}(L^1)_{12}Cl](PF_6)_3$ (12-Cl).

In the course of studying the reaction of 2-(4-dimethylaminophenyl)benzothiazoline with Cu^I ion, the recrystallization of crude sample of **9** from $CHCl_3$ led to the production of red crystals of **12-Cl** as a minor product, together with black crystals of **9**. A similar reaction using excess amount of Bu_4NCl in $CHCl_3$ gave a red powder of **12-Cl** in a moderate yield. In addition, **12-Cl** was also obtained in a higher yield by the 4:3 reaction of $[Cu(CH_3CN)_4]PF_6$ with 2-(4-dimethylaminophenyl)benzothiazoline in the presence of excess Bu_4NCl. These results imply that chloride ions acts as a template for the construction of **12-Cl**.

Unlike the absorption spectrum of **9**, no near-infrared band was observed in the absorption spectrum of **12-Cl** in CH_3CN (Figure 2-18). This is compatible with the assignment of the +1 oxidation state for all Cu atoms in **12-Cl**, with the lack of electron(s) delocalized over the S-bridged core structure.[17] The ESI mass spectrum of **12-Cl** in CH_3CN gave a cluster of signals centered at $m/z = 1371.9$, the calculated mass and the isotopic distribution of which match well with those for $[Cu_{16}(L^1)_{12}Cl]^{3+}$ (Figure 2-19). In the ^1H NMR spectrum in CD_3CN at 0°C, **12-Cl** exhibits a single set of signals, nine 1H aromatic and one 6H methyl proton signals, for twelve L^1 ligands in the complex (Figure 2-20 (a)), suggestive of the retention of the T symmetrical structure found in crystal (*vide infra*). It is noted that four pendant phenyl proton signals for L^1 ligand were observed as doublets, which suggests that the rotation of pendant groups is limited in **12-Cl** (*vide infra*).

The structure of **12-Cl** was determined by single-crystal X-ray analysis. The crystallographic data are summarized in Table 2-2. The selected bond distances and angles are summarized in Table 2-13. The structure of **12-Cl** revealed the presence of a twelfth of complex cation $[Cu_{16}(L^1)_{12}Cl]^{3+}$ and a quarter of PF_6^- anion, besides solvated MeOH in the asymmetric unit. The entire complex-cation contains sixteen Cu atoms, twelve iminothiolate ligands L^1, 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 **12-Cl** is assigned to have a +1 oxidation state. The complex-cation consists of a tetrahedral $\{Cu^I_4Cl\}^{3+}$ core (Figure 2-21 (a)), 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 $\{Cu^I_3(L^1)_3\}$ rings (Figure 2-21 (b)), in which three Cu atoms are alternately bridged by three S atoms from three L^1 ligands to form a hexagonal ring (av. Cu–S = 2.290(14) Å). The four $\{Cu^I_3(L^1)_3\}$ rings, 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 $\{Cu^I_4Cl\}^{3+}$ core through Cu–S bonds (2.3287(6) Å) to construct a whole structure (Figure 2-21 (c)). This binding fashion completes a unique *T* symmetrical 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 (Figure 2-21 (d)). As far as we know, **12-Cl** is the first structurally characterized thiolato-bridged copper(I) cluster having a hexadeca-nuclearity. Note that there exist six sets of intramolecular π-π interaction (3.63(2) Å) between *N*,*S*-chelating phenyl rings and pendent phenyl rings in the organic layer,[20] which appears to support this spherical structure. In **12-Cl**, each L^1 ligand bridges four Cu atoms using μ_3-thiolate and μ_1-imine groups. The coordination geometry of Cu^I atoms in **12-Cl** is best described as distorted ClS_3 trigonal-pyramid and NS_2 trigonal-plane for those in the tetrahedral $\{Cu^I_4Cl\}^{3+}$ core and the $\{Cu^I_3(L^1)_3\}$ rings, respectively.

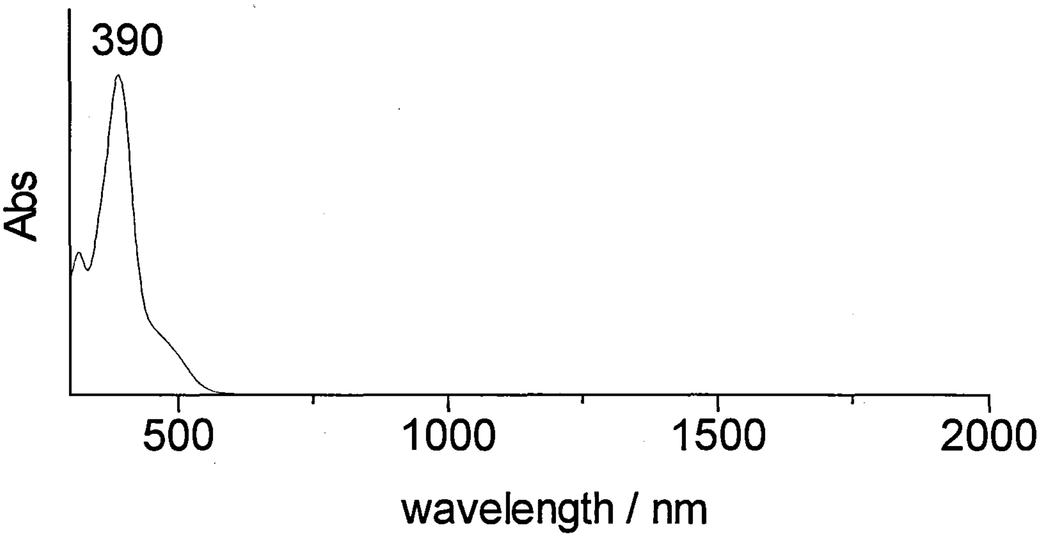


Figure 2-18. Absorption spectrum of **12-Cl** in CH_3CN.

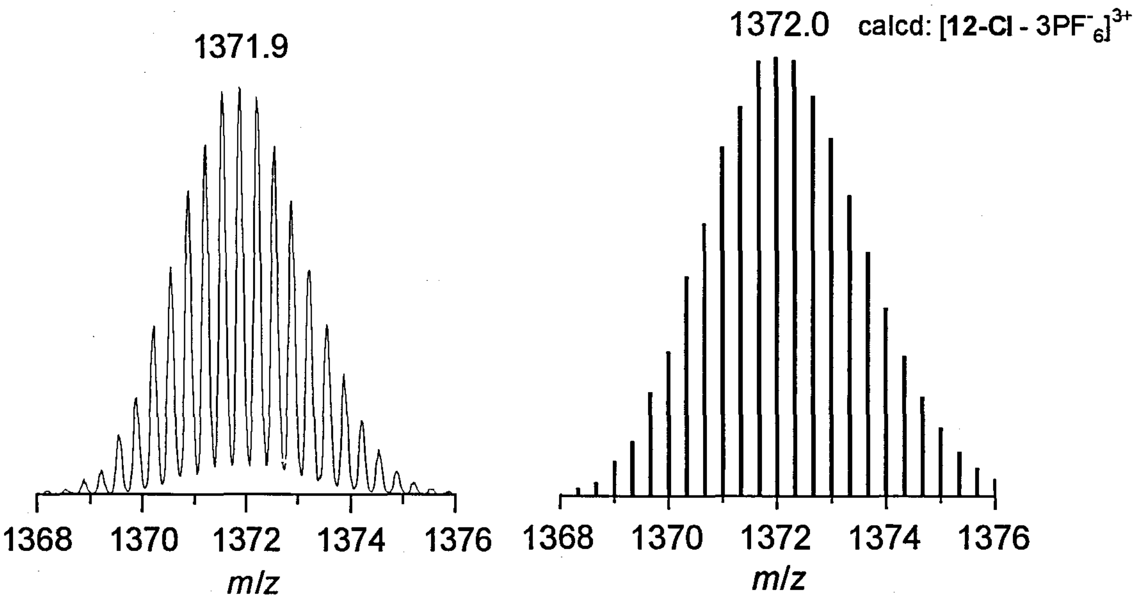


Figure 2-19. ESI mass spectrum of **12-Cl** in CH_3CN. Observed signal at *m/z* = 1371.9 (left) together with the calculated pattern for [**12-Cl** - $3PF_6^-$]$^{3+}$ (right).

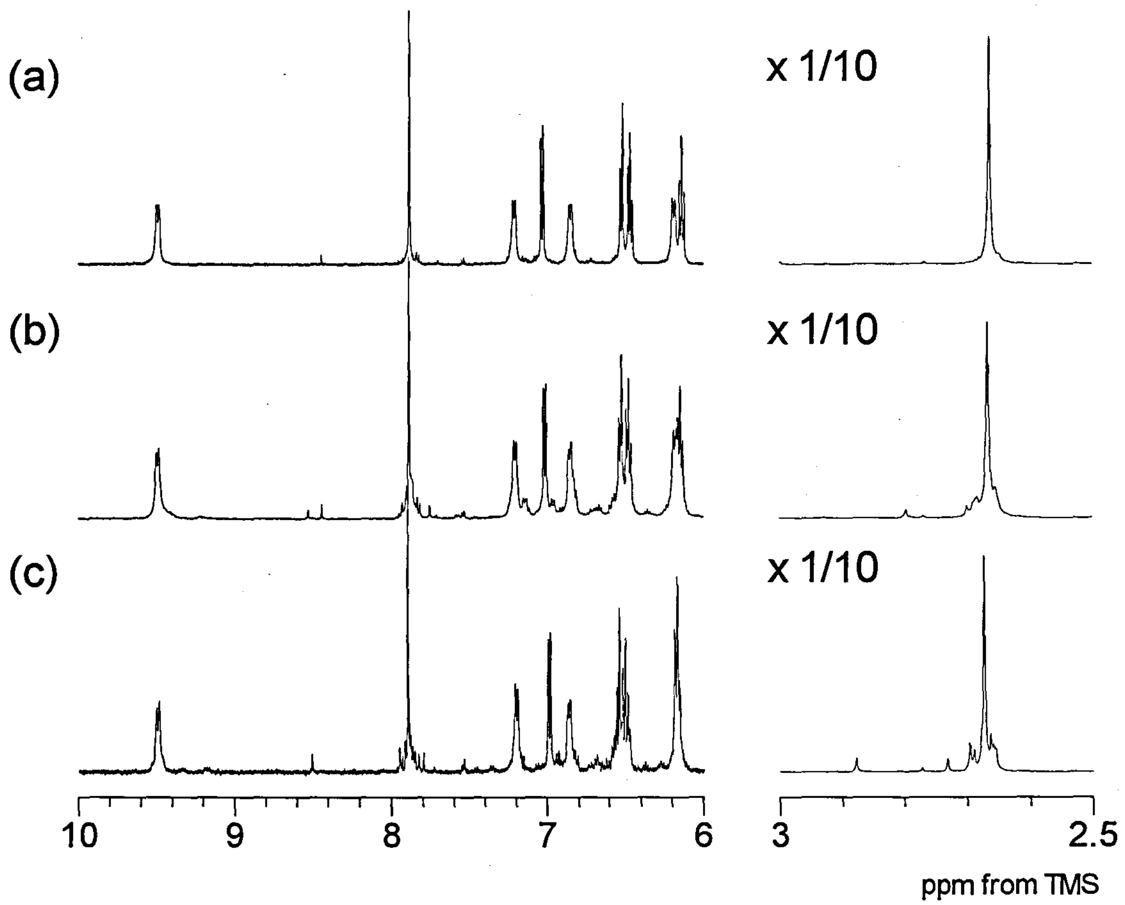


Figure 2-20. ^{1}H NMR spectra of (a) **12-Cl**, (b) **12-Br**, and (c) **12-I** in CD_3CN at 0°C.

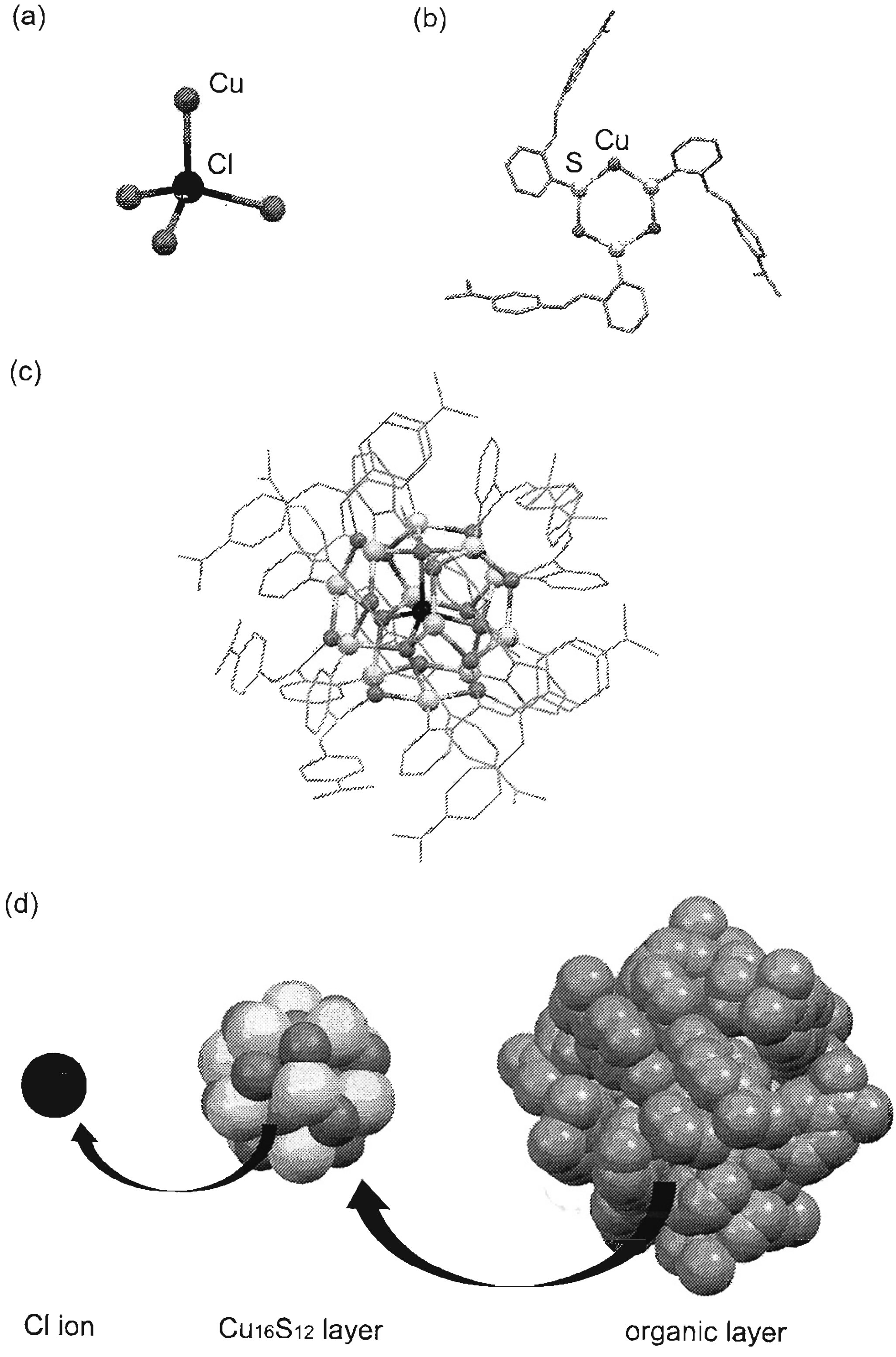


Figure 2-21. Perspective views of (a) the tetrahedral $\{Cu^{I}_{4}Cl\}^{3+}$ core, (b) the hexagonal $\{Cu^{I}_{3}(L^{1})_{3}\}$ ring, (c) the overall structure of $[Cu_{16}(L^{1})_{12}Cl]^{3+}$, and (d) space-filling model of the double-layer structure accommodating a chloride ion in **12-Cl**. Cu^{I}: dark gray, Cl: black, S: light gray, C and N: gray. H atoms are omitted for clarity.

II-3-5-2. Synthesis, structure, and characterization of $[Cu_{16}(L^1)_{12}Br](PF_6)_3$ and $[Cu_{16}(L^1)_{12}I](PF_6)_3$ (12-Br and 12-I).

When $[Cu(CH_3CN)_4]PF_6$ was treated with 2-(4-dimethylaminophenyl)benzothiazoline in a 4:3 ratio, a red powder of **12-Br** or **12-I** was obtained in a reasonable yield by adding Bu_4NBr or Bu_4NI, instead of Bu_4NCl,, respectively.

The elemental analytical data of **12-Br** and **12-I** were in agreement with the formulas for $[Cu_{16}(L^1)_{12}X](PF_6)_3$ (X = Br (**12-Br**), I (**12-I**)), and the presence of Br or I atoms in **12-Br** or **12-I** was confirmed by the fluorescence X-ray analysis. The ^1H NMR spectrum of each of **12-Br** and **12-I** in CD_3CN at 0°C gave a single set of signals, the chemical shifts of which are very similar to those for **12-Cl** (Figures 2-20 (b) and (c)). Judging from these results, together with the absence of intense near-infrared bands in their absorption spectra, **12-Br** and **12-I** are assigned to have a spherical copper(I) structure analogous to **12-Cl**.

The spherical hexadecacopper structures of **12-Br** and **12-I** were unambiguously confirmed by single-crystal X-ray analyses (Table 2-2). The selected bond distances and angles are summarized in Tables 2-14 and 2-15. The overall structure of the complex-cation ($[Cu_{16}(L^1)_{12}X]^{3+}$) in each of **12-Br** and **12-I** is very similar to that in **12-Cl**, except the presence of Br^- or I^- in place of Cl^- in **12-Cl** (Figures 2-22 and 2-23). As expected, the Cu–X bond distances increase in the order of X = Cl^- (2.4991(5) Å), Br^- (2.5819(4) Å), and I^- (2.6589(8) Å). However, the difference is rather small relative to that in the ionic radius between the halide ions (Cl^- = 1.81 Å, Br^-= 1.96 Å, and I^- = 2.20 Å).[21] In addition, the distances between the central halide ion and the center of each $\{Cu^I_3S_3\}$ ring in **12-Cl** (3.007(1) Å), **12-Br** (3.001(2) Å) and **12-I** (3.025(5) Å) are essentially the same as each other. Thus, the size of the $\{Cu^I_{16}S_{12}\}$ sphere is little affected by the accommodated halide ion. This is most likely due to the presence of the outer organic layer, the size of which is predetermined by the multiple intramolecular π-π interactions. To our best knowledge, this is the first demonstration of an expansion of high-nuclear structures by halide ions for copper-thiolate systems.

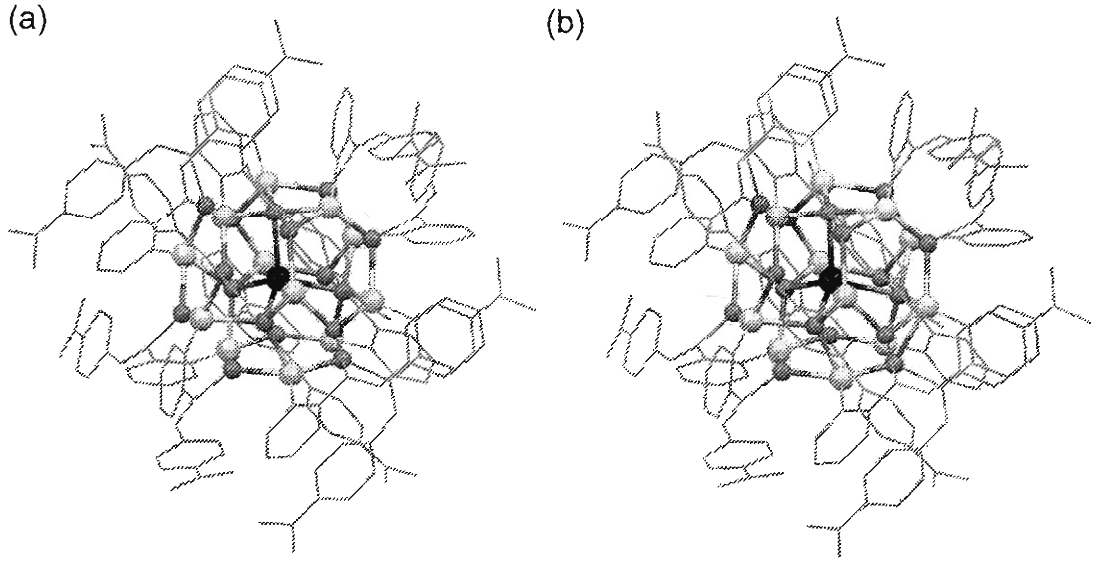


Figure 2-22. Perspective views of (a) **12-Br** and (b) **12-I**. Cu^I: dark gray, Br and I: black, S: light gray, C and N: gray (wireframe). H atoms are omitted for clarity.

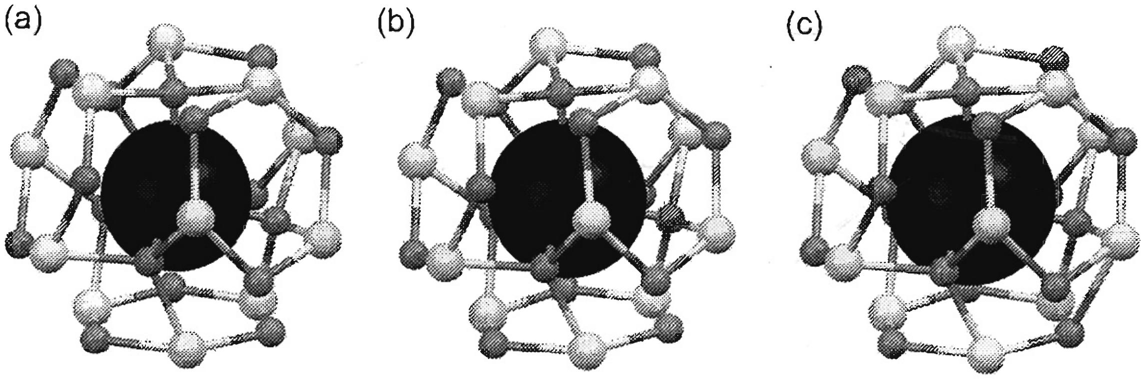


Figure 2-23. Perspective views of the $\{Cu^I_{16}S_{12}X\}^{3+}$ core structures in (a) **12-Cl**, (b) **12-Br**, and (c) **12-I**. Cu^I: dark gray, Cl, Br, and I: black, S: light gray.

II-3-5-3. Template effect of halide ions.

As shown in II-3-5-1 and II-3-5-2, it was demonstrated that the reaction of 2-(4-dimethylaminophenyl)benzothiazoline with copper(I) ion in the presence of halide ion gave the hexadecanuclear copper(I) cluster having a central halide ion, $[Cu_{16}(L^1)_{12}X]^{3+}$ (**12-X**), while a similar reaction in the absence of halide ions gave the cyclic octanuclear copper cluster, $[Cu_8(L^1)_8]^{2+}$ (**9**), as described in II-3-3. These results imply the presence of template effect of halide ions on the Cu^I-benzothiazoline system.

To obviously establish the template effect due to Cl^- ion, the 4:3 reaction solution of $[Cu(CH_3CN)_4]PF_6$ and 2-(4-dimethylaminophenyl)benzothiazoline in CD_3OD/CD_3CN was carried out. The ^1H NMR spectrum before adding Bu_4NCl showed complicated, multiple proton signals, while a single set of signals for **12-Cl** appeared dominantly in the ^1H NMR spectrum after adding Bu_4NCl (Figure 2-24). This result clearly showed that chloride ions act as a template for the construction of $[Cu_{16}(L^1)_{12}Cl]^{3+}$ and that the octa- and hexadecanuclear copper structures are controlled by the presence/absence of halide ions (Scheme 2-4). As far as we know, this is the first example of the high nuclear copper-thiolato system that is controlled by template effect of halide ion.

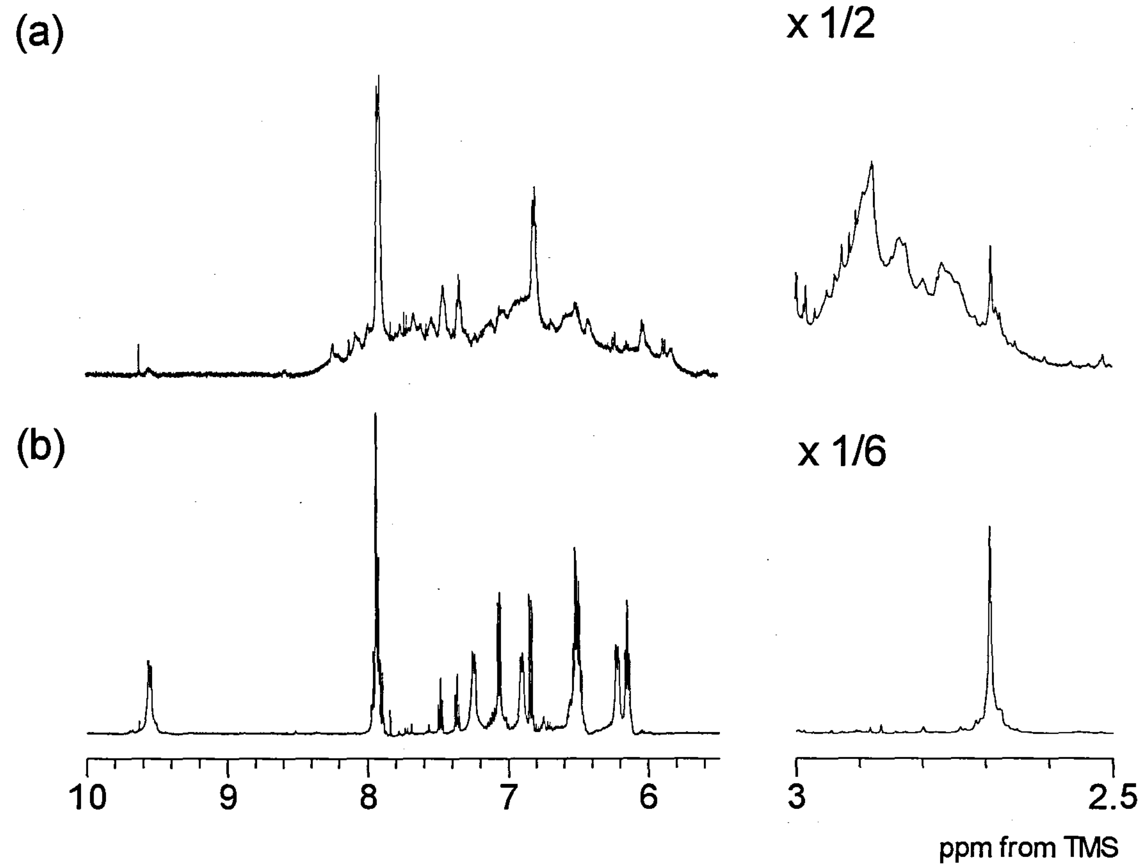
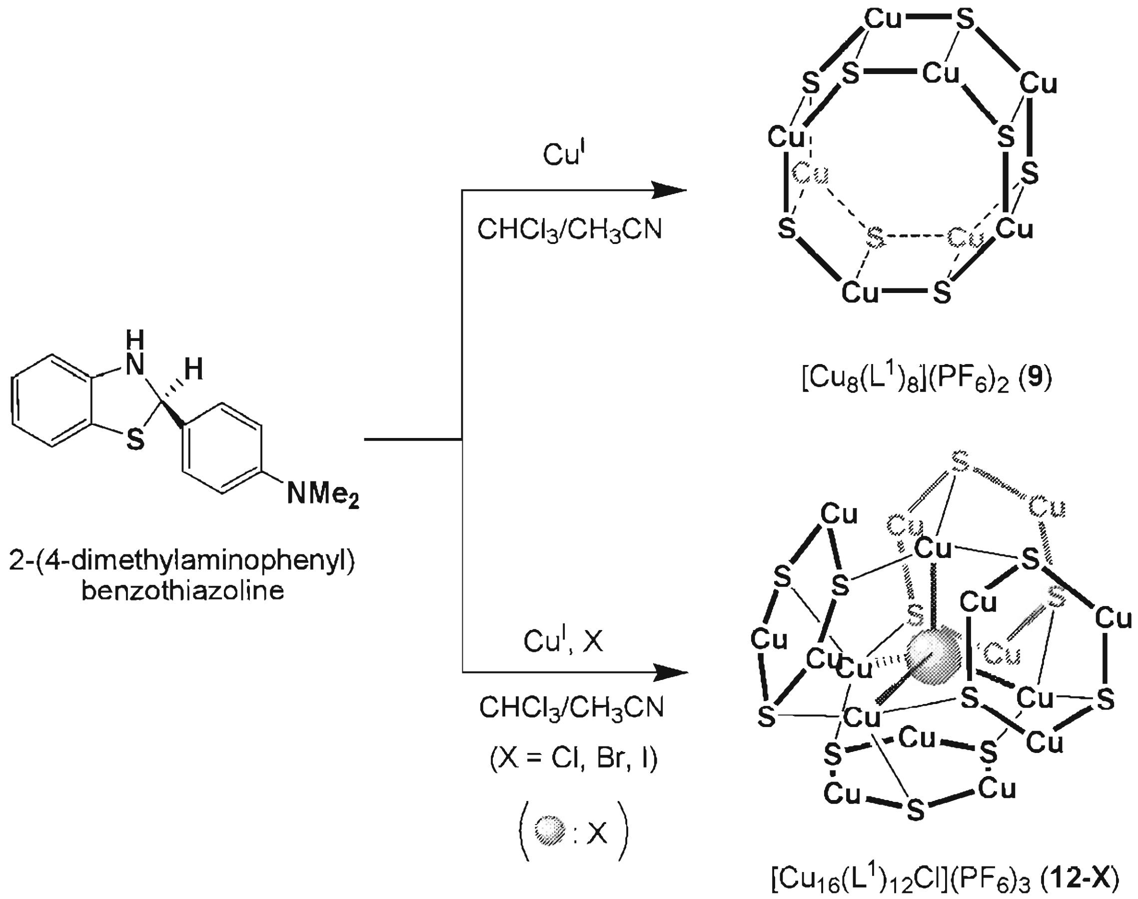


Figure 2-24. (a) ^{1}H NMR spectra of a 4:3 reaction mixture of $[Cu(CH_3CN)_4]PF_6$ and 2-(4-dimethylaminophenyl)benzothiazoline before adding Bu_4NCl and (b) that after adding Bu_4NCl in CD_3OD/CD_3CN at 0°C.



Scheme 2-4. Syntheses of octa- and hexadecanuclear $\mathrm{Cu^I}$ cluster $[\mathrm{Cu_8(L^1)_8}](\mathrm{PF_6})_2$ (**9**) and $[\mathrm{Cu_{16}(L^1)_{12}X}](\mathrm{PF_6})_3$ (**12-X**) (X = Cl, Br, I).

II-4. Summary.

In this chapter, the coordination behavior of iminothiophenolate ligands derived from benzothiazolines toward the d^{10} ions of the group 11 elements were investigated. The influence of substituent groups of the ligands and the reacting metal centers on the resulting multinuclear complexes were clarified. Moreover, the template effect of halide ions was investigated in detail, especially for Cu^I-L^1 system.

For the reactions of Au^I or Ag^I ions with benzothiazolines, μ_2-S-bridged tetranuclear metallorings with an 8-membered cyclic core $[M_4L_4]$, in which each thiolate group bridges two Au^I or Ag^I atoms, were commonly formed. In the Au^I_4 metallorings, each iminothiophenolate ligand binds to metal centers only through its thiolato group to adopt a μ_2-κ^1S:κ^1S coordination mode. On the other hand, each iminothiophenolate ligand adopts a μ_2-κ^1S:κ^2N,S coordination mode in the Ag^I_4 metallorings, in which its imine group weakly coordinates to an Ag^I atom. Although analogous thiophenolate-bridged tetrasilver(I) rings have been reported,[6d,e] **1** and **2** are the first example of thiophenolate-bridged cyclic tetragold(I) complexes bearing an almost regular square-planar $\{Au^I_4S_4\}$ ring.

It was found that the reactions of benzothiazolines with Cu^I ions gave μ_2- or μ_3-S-bridged multinuclear complexes with various nuclearities, $[Cu_3(L^2)_3]$, $[Cu_4(L^4)_4]$, $[Cu_8(L^1)_8]^{2+}$, $[Cu_{10}(L^1)_9]$, and $[Cu_{16}(L^1)_{12}X]^{3+}$ ($X = Cl^-$, Br^-, and I^-), which are composed of $\{Cu^I_3S_3\}$ or $\{Cu^I_4S_4\}$ metalloring moieties. The structures of Cu^I complexes were found to be highly sensitive to the bulkiness of the substituent group. This is in sharp contrast to the less sensitive Au^I and Ag^I systems. Moreover, the coordination systems derived from Cu^I ion and L^1 ligand showed the halide-template formation of S-bridged spherical clusters. To our knowledge, this is the first systematic study on the syntheses and structures of Au^I, Ag^I, and Cu^I complexes having iminothiophenolate ligands.

II-5. References.

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Table 2-1. Crystallographic data of **1**-**7**.

	1·$CHCl_3$	**2**	**3**·$CHCl_3$	**4**	**5**·2$CHCl_3$	**6**·2$CHCl_3$	**7**·2$CHCl_3$
empirical formula	$C_{61}H_{61}Au_4Cl_3N_8S_4$	$C_{64}H_{64}Au_4N_4S_4$	$C_{61}H_{61}Ag_4Cl_3N_8S_4$	$C_{64}H_{64}Ag_4N_4S_4$	$C_{70}H_{50}Ag_4Cl_6N_4S_4$	$C_{86}H_{58}Ag_4Cl_6N_4S_4$	$C_{58}H_{50}Ag_4Cl_6N_4O_4S_4$
fw	1928.63	1805.30	1572.25	1448.91	1719.56	1919.78	1639.44
size /mm^3	0.09×0.09×0.02	0.15×0.15× 0.10	0.23×0.20×0.15	0.20×0.10×0.01	0.20×0.07×0.05	0.13×0.10×0.10	0.50×0.06×0.03
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group	$C2/c$	P-1	$P2_1/n$	P-1	P-1	$C2/c$	P-1
a /Å	25.778(7)	11.0280(4)	14.318(4)	10.2638(4)	11.311(5)	26.440(3)	8.135(2)
b /Å	14.648(3)	11.7442(5)	13.123(3)	10.4736(4)	12.092(5)	12.9461(15)	13.484(4)
c /Å	16.767(4)	12.0057(5)	17.076(5)	15.6692(5)	12.521(5)	23.168(2)	15.915(6)
α /°		69.7860(10)		99.545(7)	96.418(13)		114.177(10)
β /°	101.212(10)	83.0280(10)	106.829(12)	98.031(7)	104.074(15)	105.862(7)	90.055(11)
γ /°		87.8320(10)		113.028(8)	104.337(16)		100.953(9)
V /Å^3	6210(3)	1448.35(10)	3071.1(13)	1489.39(15)	1582.3(11)	7628.5(15)	1557.6(8)
Z	4	1	2	1	1	4	1
T /K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
R(int)	0.0990	0.0761	0.0627	0.0230	0.0865	0.0827	0.0433
$\rho_{calcd.}$ /g cm^{-3}	2.063	2.070	1.700	1.615	1.805	1.672	1.748
μ (Mo Ka), mm^{-1}	9.729	10.286	1.569	1.479	1.653	1.381	1.678
θ_{Max}	55.0	54.9	54.9	54.9	55.0	54.9	55.0
R_1 (I>2σ(I))^a	0.045	0.044	0.036	0.058	0.055	0.048	0.040
Rw^b	0.146	0.112	0.075	0.148	0.173	0.120	0.114

[a] $R_1 = \Sigma|(|F_o|-|F_c|)| / \Sigma(|F_o|)$. [b] $Rw = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2-2. Crystallographic data of **8-12**.

	8·$CHCl_3$·$8H_2O$	**10**·$0.5CH_2Cl_2$	**11**·$2CHCl_3$	**12-Cl**·6MeOH	**12-Br**·6MeOH	**12-I**·6MeOH
empirical formula	$C_{136}H_{136}Cl_3Cu_{10}N_{18}O_8S_9$	$C_{48.5}H_{49}ClCu_3N_3S_3$	$C_{86}H_{58}Cl_6Cu_4N_4S_4$	$C_{186}H_{204}ClCu_{16}F_{18}N_{24}O_6P_3S_{12}$	$C_{186}H_{204}BrCu_{16}F_{18}N_{24}O_6P_3S_{12}$	$C_{186}H_{204}ICu_{16}F_{18}N_{24}O_6P_3S_{12}$
fw	3180.92	996.16	1742.46	4743.45	4787.91	4834.90
size /mm^3	0.10×0.10×0.10	0.40×0.08×0.04	0.15×0.15×0.10	0.30×0.30×0.20	0.30×0.30×0.20	0.15×0.15×0.05
crystal system	triclinic	monoclinic	monoclinic	cubic	cubic	cubic
space group	*P*-1	$P2_1/n$	*C*2/*c*	*Fd*-3*c*	*Fd*-3*c*	*Fd*-3*c*
a /Å	17.1100(9)	13.7846(4)	25.8476(12)	43.5328(8)	44.0618(6)	44.2098(16)
b /Å	21.8363(6)	11.1736(4)	12.9160(5)			
c /Å	25.8606(8)	30.9608(9)	22.9699(11)			
α /°	81.078(6)					
β /°	72.904(5)	95.4130(10)	106.0460(10)			
γ /°	74.078(5)					
V /Å^3	8851.6(6)	4747.4(3)	7369.7(6)	82499(5)	85543(2)	86408(9)
Z	2	4	4	16	16	16
T /K	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
R(int)	0.1168	0.0866	0.0613	0.1356	0.0583	0.1487
$\rho_{calcd.}$ /g cm^{-3}	1.193	1.394	1.570	1.528	1.487	1.487
μ (Mo Ka), mm^{-1}	1.376	1.555	1.521	1.843	1.952	1.890
θ_{Max}	55.0	54.9	55.0	55.0	54.9	55.0
R_1 $(I>2\sigma(I))^a$	0.200	0.059	0.046	0.056	0.041	0.070
Rw^b	0.552	0.217	0.121	0.165	0.139	0.208

[a] $R_1 = \Sigma|(|F_o|-|F_c|)| / \Sigma(|F_o|)$. [b] $Rw = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 2-3. Selected bond distances and angles of **1**·$CHCl_3$.

	Bond distances (Å)		
Au(1)-S(1)	2.305(2)	Au(2)-N(1)	3.047(2)
Au(1)-S(2)	2.318(2)	Au(2)#1-N(3)	3.146(2)
Au(2)-S(1)	2.309(2)	Au(1)-Au(2)#1	3.1872(9)
Au(2)-S(2)#1	2.311(2)	Au(1)-Au(2)	3.3706(9)
Au(1)-N(3)	3.279(2)		
	Angles (°)		
S(1)-Au(1)-S(2)	174.98(8)	Au(1)-S(1)-Au(2)	93.84(8)
S(1)-Au(2)-S(2)#1	179.15(8)	Au(2)#1-S(2)-Au(1)	87.02(7)

#1 -x+1/2,-y+1/2,-z

Table 2-4. Selected bond distances and angles of **2**.

	Bond distances (Å)		
Au(1)-S(1)	2.3038(16)	Au(2)-S(2)#1	2.3040(16)
Au(1)-S(2)	2.3185(15)	Au(1)-Au(2)	3.3199(4)
Au(2)-S(1)	2.3014(17)	Au(1)-Au(2)#1	3.1367(3)
	Angles (°)		
S(1)-Au(1)-S(2)	173.58(6)	Au(1)-S(1)-Au(2)	92.26(5)
S(1)-Au(2)-S(2)#1	171.51(6)	Au(1)-S(2)-Au(2)#1	85.46(5)

#1 -x+2,-y+1,-z

Table 2-5. Selected bond distances and angles of **3**·$CHCl_3$.

	Bond distances (Å)		
Ag(1)-S(1)	2.4458(9)	Ag(1)-N(1)	2.554(2)
Ag(1)-S(2)	2.4508(9)	Ag(1)-N(3)	2.701(3)
Ag(2)-S(1)	2.3926(8)	Ag(1)-Ag(2)#1	3.0124(8)
Ag(2)-S(2)#1	2.4099(9)		
	Angles (°)		
S(1)-Ag(1)-S(2)	145.37(3)	Ag(1)-S(1)-Ag(2)	102.13(3)
S(1)-Ag(2)-S(2)#1	166.84(3)	Ag(1)-S(2)-Ag(2)#1	76.59(3)

#1 -x+2,-y,-z+1

Table 2-6. Selected bond distances and angles of **4**.

Bond distances (Å)			
Ag(1)-S(1)	2.3876(14)	Ag(2)-N(1)	2.575(6)
Ag(1)-S(2)	2.4136(15)	Ag(1)-N(2)	2.572(4)
Ag(2)-S(2)#1	2.3718(16)	Ag(1)-Ag(2)	3.1153(7)
Ag(2)-S(1)	2.4192(16)		
Angles (°)			
S(1)-Ag(1)-S(2)	161.03(5)	Ag(1)-S(1)-Ag(2)	80.79(5)
S(2)#1-Ag(2)-S(1)	169.78(5)	Ag(1)-S(2)-Ag(2)#1	97.20(6)

#1 -x+1,-y+1,-z+1

Table 2-7. Selected bond distances and angles of **5**·2$CHCl_3$.

Bond distances (Å)			
Ag(1)-S(1)	2.4050(18)	Ag(1)-N(2)	2.603(5)
Ag(1)-S(2)	2.4531(18)	Ag(1)-N(1)	2.815(5)
Ag(2)-S(2)	2.3985(16)	Ag(1)-Ag(2)	3.0988(11)
Ag(2)-S(1)#1	2.3813(17)		
Angles (°)			
S(1)-Ag(1)-S(2)	149.88(5)	Ag(1)-S(2)-Ag(2)	79.38(5)
S(1)#1-Ag(2)-S(2)	167.05(6)	Ag(1)-S(1)-Ag(2)#1	93.67(6)

#1 -x+1,-y+1,-z+1

Table 2-8. Selected bond distances and angles of **6**·2$CHCl_3$.

Bond distances (Å)			
Ag(1)-S(1)	2.4572(11)	Ag(1)-N(1)	2.483(3)
Ag(1)-S(2)	2.4884(11)	Ag(1)-N(2)	2.449(3)
Ag(2)-S(1)	2.3531(12)	Ag(1)-Ag(2)#1	2.8569(6)
Ag(2)-S(2)#1	2.3824(12)		
Angles (°)			
S(1)-Ag(1)-S(2)	146.71(4)	Ag(1)-S(1)-Ag(2)	122.90(5)
S(1)-Ag(2)-S(2)#1	166.79(4)	Ag(1)-S(2)-Ag(2)#1	71.78(3)

#1 -x+1,-y,-z

Table 2-9. Selected bond distances and angles of **7**·$2CHCl_3$.

	Bond distances (Å)		
Ag(1)-S(1)	2.3906(12)	Ag(1)-N(1)	2.802(4)
Ag(1)-S(2)	2.3951(13)	Ag(2)-N(2)#1	2.573(3)
Ag(2)-S(1)	2.3771(13)	Ag(1)-Ag(2)#1	3.1636(8)
Ag(2)-S(2)#1	2.4227(13)		
	Angles (°)		
S(1)-Ag(1)-S(2)	168.60(4)	Ag(2)-S(1)-Ag(1)	91.05(4)
S(1)-Ag(2)-S(2)#1	159.60(4)	Ag(1)-S(2)-Ag(2)#1	82.09(4)

#1 -x+1,-y,-z

Table 2-10. Selected bond distances and angles of $\mathbf{8}\cdot \mathrm{CHCl_3}\cdot 8\mathrm{H_2O}$.

Bond distances (Å)

Cu(1)-S(1)	2.291(5)	Cu(9)-S(2)	2.326(5)
Cu(1)-S(2)	2.275(6)	Cu(9)-S(7)	2.329(5)
Cu(1)-S(3)	2.278(5)	Cu(10)-S(3)	2.300(5)
Cu(2)-S(1)	2.303(6)	Cu(10)-S(8)	2.306(6)
Cu(2)-S(4)	2.251(6)	Cu(5)-N(11)	2.035(17)
Cu(2)-S(7)	2.212(5)	Cu(6)-N(7)	2.039(18)
Cu(3)-S(2)	2.281(6)	Cu(7)-N(9)	2.07(2)
Cu(3)-S(5)	2.210(8)	Cu(8)-N(1)	2.144(19)
Cu(3)-S(8)	2.243(7)	Cu(8)-N(17)	2.081(17)
Cu(4)-S(3)	2.260(5)	Cu(9)-N(3)	2.170(17)
Cu(4)-S(6)	2.249(6)	Cu(9)-N(13)	2.104(19)
Cu(4)-S(9)	2.219(6)	Cu(10)-N(5)	2.076(19)
Cu(5)-S(4)	2.173(6)	Cu(10)-N(15)	2.11(2)
Cu(5)-S(6)	2.310(6)	Cu(1)-Cu(2)	2.957(3)
Cu(6)-S(4)	2.308(6)	Cu(1)-Cu(3)	3.035(4)
Cu(6)-S(5)	2.202(6)	Cu(1)-Cu(4)	3.001(4)
Cu(7)-S(5)	2.344(7)	Cu(2)-Cu(9)	2.840(3)
Cu(7)-S(6)	2.173(6)	Cu(3)-Cu(10)	2.863(4)
Cu(8)-S(1)	2.295(6)	Cu(4)-Cu(8)	2.911(3)
Cu(8)-S(9)	2.357(6)	Cu(6)-Cu(7)	3.044(4)

Angles (°)

S(1)-Cu(1)-S(2)	121.4(2)	Cu(2)-S(1)-Cu(8)	146.8(3)
S(1)-Cu(1)-S(3)	120.2(2)	Cu(1)-S(2)-Cu(3)	83.6(2)
S(2)-Cu(1)-S(3)	117.4(2)	Cu(1)-S(2)-Cu(9)	113.0(2)
S(1)-Cu(2)-S(4)	115.8(2)	Cu(3)-S(2)-Cu(9)	145.5(3)
S(1)-Cu(2)-S(7)	115.7(2)	Cu(1)-S(3)-Cu(4)	82.81(17)
S(4)-Cu(2)-S(7)	128.3(2)	Cu(1)-S(3)-Cu(10)	118.6(3)
S(2)-Cu(3)-S(5)	111.2(2)	Cu(4)-S(3)-Cu(10)	141.1(3)
S(2)-Cu(3)-S(8)	116.9(3)	Cu(2)-S(4)-Cu(5)	118.9(3)
S(5)-Cu(3)-S(8)	131.8(2)	Cu(2)-S(4)-Cu(6)	127.6(3)
S(3)-Cu(4)-S(6)	114.3(2)	Cu(5)-S(4)-Cu(6)	86.3(2)
S(3)-Cu(4)-S(9)	112.5(2)	Cu(3)-S(5)-Cu(6)	121.8(3)
S(6)-Cu(4)-S(9)	133.2(2)	Cu(3)-S(5)-Cu(7)	129.0(3)
S(4)-Cu(5)-S(6)	118.5(2)	Cu(6)-S(5)-Cu(7)	84.0(2)
S(4)-Cu(6)-S(5)	118.9(2)	Cu(4)-S(6)-Cu(5)	129.6(3)
S(5)-Cu(7)-S(6)	117.9(2)	Cu(4)-S(6)-Cu(7)	118.6(2)
S(1)-Cu(8)-S(9)	124.04(19)	Cu(5)-S(6)-Cu(7)	86.2(2)
S(2)-Cu(9)-S(7)	124.5(2)	Cu(2)-S(7)-Cu(9)	77.38(16)
S(3)-Cu(10)-S(8)	121.2(2)	Cu(3)-S(8)-Cu(10)	78.0(2)
Cu(1)-S(1)-Cu(2)	80.15(19)	Cu(4)-S(9)-Cu(8)	78.95(19)
Cu(1)-S(1)-Cu(8)	112.9(2)		

Table 2-11. Selected bond distances and angles of **10**·$0.5CH_2Cl_2$.

	Bond distances (Å)		
Cu(1)-S(1)	2.2761(14)	Cu(1)-N(1)	2.083(4)
Cu(1)-S(2)	2.1974(13)	Cu(2)-N(3)	2.098(4)
Cu(2)-S(1)	2.2189(13)	Cu(3)-N(2)	2.085(4)
Cu(2)-S(3)	2.2412(13)	Cu(1)-Cu(2)	2.5561(8)
Cu(3)-S(2)	2.2841(13)	Cu(1)-Cu(3)	2.7447(8)
Cu(3)-S(3)	2.2060(12)	Cu(2)-Cu(3)	2.6680(7)
	Angles (°)		
S(1)-Cu(1)-S(2)	146.07(6)	Cu(1)-S(1)-Cu(2)	69.30(4)
S(1)-Cu(2)-S(3)	150.48(6)	Cu(1)-S(2)-Cu(3)	75.51(4)
S(2)-Cu(3)-S(3)	144.15(5)	Cu(2)-S(3)-Cu(3)	73.73(4)

Table 2-12. Selected bond distances and angles of **11**·$2CHCl_3$.

	Bond distances (Å)		
Cu(1)-S(2)	2.2812(8)	Cu(1)-N(1)	2.122(3)
Cu(1)-S(1)	2.2925(8)	Cu(1)-N(2)	2.132(2)
Cu(2)-S(1)	2.1713(8)	Cu(1)-Cu(2)	2.6095(5)
Cu(2)-S(2)#1	2.1504(8)		
	Angles (°)		
S(1)-Cu(1)-S(2)	133.22(3)	Cu(1)-S(1)-Cu(2)	71.49(3)
S(1)-Cu(2)-S(2)#1	169.40(4)	Cu(1)-S(2)-Cu(2)#1	130.88(4)

#1 -x,-y+1,-z

Table 2-13. Selected bond distances and angles of **12-Cl**·6MeOH.

	Bond distances (Å)		
Cu(1)-S(1)#1	2.3286(6)	Cu(2)-S(1)#3	2.2765(7)
Cu(1)-S(1)	2.3286(6)	Cu(2)-S(1)#1	2.3038(7)
Cu(1)-S(1)#2	2.3287(6)	Cu(2)-S(1)	2.7363(7)
Cu(1)-Cl(1)	2.4991(5)	Cu(2)-Cu(2)#3	2.8786(6)
Cu(1)-Cu(2)	2.6969(3)	Cl(1)-Cu(1)#4	2.4989(5)
Cu(1)-Cu(2)#2	2.6970(3)	Cl(1)-Cu(1)#5	2.4990(5)
Cu(1)-Cu(2)#1	2.6971(3)	Cl(1)-Cu(1)#6	2.4990(5)
Cu(2)-N(1)	2.004(2)		
	Angles (°)		
S(1)#1-Cu(1)-S(1)	116.122(13)	S(1)#3-Cu(2)-S(1)	107.60(2)
S(1)#1-Cu(1)-S(1)#2	116.122(13)	S(1)#1-Cu(2)-S(1)	102.95(3)
S(1)-Cu(1)-S(1)#2	116.130(13)	Cu(1)#4-Cl(1)-Cu(1)#5	109.471(1)
S(1)#1-Cu(1)-Cl(1)	101.51(2)	Cu(2)#3-S(1)-Cu(2)#2	125.43(3)
S(1)-Cu(1)-Cl(1)	101.50(2)	Cu(2)#3-S(1)-Cu(1)	108.42(3)
S(1)#2-Cu(1)-Cl(1)	101.50(2)	Cu(2)#2-S(1)-Cu(1)	71.20(2)
N(1)-Cu(2)-S(1)#3	121.61(6)	Cu(2)#3-S(1)-Cu(2)	69.40(2)
N(1)-Cu(2)-S(1)#1	119.40(6)	Cu(2)#2-S(1)-Cu(2)	134.85(3)
S(1)#3-Cu(2)-S(1)#1	114.58(3)	Cu(1)-S(1)-Cu(2)	63.749(16)
N(1)-Cu(2)-S(1)	80.84(6)		

#1 z,-x+1/4,-y+1/4 #2 -y+1/4,-z+1/4,x #3 -x+1/4,y,-z+1/4 #4 -y+1/4,z,-x+1/4
#5 -z+1/4,-x+1/4,y #6 -z+1/4,x,-y+1/4 #7 y-1/4,x+1/4,-z

Table 2-14. Selected bond distances and angles of **12-Br**·6MeOH.

Bond distances (Å)			
Cu(1)-S(1)#1	2.3200(4)	Cu(2)-Cu(2)#3	2.8432(5)
Cu(1)-S(1)#2	2.3201(4)	Br(1)-Cu(1)#4	2.5817(4)
Cu(1)-S(1)	2.3202(4)	Br(1)-Cu(1)#5	2.5817(4)
Cu(1)-Br(1)	2.5819(4)	Br(1)-Cu(1)#6	2.5817(4)
Cu(2)-N(1)	2.0083(16)	S(1)-C(1)	1.7950(19)
Cu(2)-S(1)#3	2.2864(5)	S(1)-Cu(2)#3	2.2863(5)
Cu(2)-S(1)#2	2.3149(5)	S(1)-Cu(2)#1	2.3148(5)
Cu(2)-S(1)	2.7160(5)		
Angles (°)			
S(1)#1-Cu(1)-S(1)#2	117.302(8)	N(1)-Cu(2)-S(1)#2	119.04(5)
S(1)#1-Cu(1)-S(1)	117.301(8)	S(1)#3-Cu(2)-S(1)#2	113.85(2)
S(1)#2-Cu(1)-S(1)	117.303(8)	N(1)-Cu(2)-S(1)	81.13(5)
S(1)#1-Cu(1)-Br(1)	99.554(14)	S(1)#3-Cu(2)-S(1)	108.349(15)
S(1)#2-Cu(1)-Br(1)	99.554(14)	S(1)#2-Cu(2)-S(1)	103.66(2)
S(1)-Cu(1)-Br(1)	99.554(14)	Cu(1)-Cu(2)-S(1)	50.923(10)
N(1)-Cu(2)-S(1)#3	121.97(5)	Cu(1)#4-Br(1)-Cu(1)#5	109.471(1)

#1 -y+1/4,-z+1/4,x #2 z,-x+1/4,-y+1/4 #3 -x+1/4,y,-z+1/4 #4 -y+1/4,z,-x+1/4
#5 -z+1/4,-x+1/4,y #6 -z+1/4,x,-y+1/4 #7 y-1/4,x+1/4,-z

Table 2-15. Selected bond distances and angles of **12-I**·6MeOH.

	Bond distances (Å)		
Cu(1)-S(1)	2.3387(9)	Cu(2)-S(1)	2.7248(10)
Cu(1)-S(1)#1	2.3387(9)	I(1)-Cu(1)#4	2.6588(8)
Cu(1)-S(1)#2	2.3388(9)	I(1)-Cu(1)#5	2.6588(8)
Cu(1)-I(1)	2.6589(8)	I(1)-Cu(1)#6	2.6589(8)
Cu(2)-N(1)	2.014(3)	S(1)-Cu(2)#3	2.3115(10)
Cu(2)-S(1)#3	2.3118(10)	S(1)-Cu(2)#2	2.3437(10)
Cu(2)-S(1)#1	2.3436(10)		
	Angles (°)		
S(1)-Cu(1)-S(1)#1	117.815(14)	S(1)#3-Cu(2)-S(1)	108.66(3)
S(1)-Cu(1)-S(1)#2	117.813(14)	S(1)#1-Cu(2)-S(1)	104.17(4)
S(1)#1-Cu(1)-S(1)#2	117.819(15)	Cu(1)-Cu(2)-S(1)	51.17(2)
S(1)-Cu(1)-I(1)	98.58(3)	Cu(2)#3-S(1)-Cu(1)	109.89(4)
S(1)#1-Cu(1)-I(1)	98.58(3)	Cu(2)#3-S(1)-Cu(2)#2	125.25(4)
S(1)#2-Cu(1)-I(1)	98.58(3)	Cu(1)-S(1)-Cu(2)#2	70.13(3)
N(1)-Cu(2)-S(1)#3	121.56(10)	Cu(2)#3-S(1)-Cu(2)	68.72(3)
N(1)-Cu(2)-S(1)#1	118.36(9)	Cu(1)-S(1)-Cu(2)	63.65(2)
S(1)#3-Cu(2)-S(1)#1	114.69(4)	Cu(2)#2-S(1)-Cu(2)	133.41(4)
N(1)-Cu(2)-S(1)	80.58(10)		

#1 z,-x+1/4,-y+1/4 #2 -y+1/4,-z+1/4,x #3 -x+1/4,y,-z+1/4 #4 -z+1/4,-x+1/4,y

#5 -z+1/4,x,-y+1/4 #6 -y+1/4,z,-x+1/4 #7 y-1/4,x+1/4,-z

Chapter III.
Heterometallic Complexes Derived from Benzothiazolines.

III-1. Introduction.

The design and synthesis of metal-containing molecular rings have been an active area of research in the field of coordination chemistry and supramolecular chemistry because of their architectural beauty and often their intriguing properties.[1] The common approach to create such metallorings is the linkage of rigid organic ligands with transition metal ions/complexes in a closed form through self-assembly processes; a large number of molecular rings with M–N, M–O, M–P, and M–S coordination bonds have so far been prepared by this approach.[2–4] This approach is beneficial for the construction of homometallic ring structures consisting of metal-ligand repeating units, denoted as $\{ML\}_n$, the ring size of which can be controlled by the number and length of the units.[3] In particular, thiolato-bridged metalloring structures of $[M(SR)]_n$ type are well known.[4] In contrast, it is not straightforward to prepare heterometallic molecular rings, in which two or more different metal ions are precisely positioned, by the simple self-assembly approach of a single kind of ligands in combination with different kinds of metal ions. To date, only a relatively small number of heterometallic molecular rings has appeared in the literature,[5,6] and thus, the finding of a methodology that allows the selective formation of heterometallic molecular rings in a rational manner is a key concern in this research area.

In Chapter II, it was found that the reactions of benzothiazolines with the d^{10} ions of the group 11 elements commonly form the $\{ML\}_n$ metalloring structures, in which iminothiophenolate ligands bridge d^{10} metal ions through thiophenolate groups. In the homometallic Au^I metallorings, each of Au^I center was always coordinated by two thiophenolato groups, adopting a two-coordinated linear geometry. On the other hand, Ag^I and Cu^I centers were coordinated by imino groups in addition to the thiophenolato groups in some cases, forming two-coordinated linear-type, three coordinated T-shape, and four-coordinated tetrahedral geometries. Thus, the imino donors of iminothiophenolate ligands remain uncoordinated in the homometallic Au^I rings, while the coordination sites of Ag^I and Cu^I centers are not saturated in the homometallic Ag^I and Cu^I rings. Based on this result, it is expected that heterometallic molecular rings with a maximum number of coordination bonds will be selectively formed if two kinds of d^{10} metal ions react with benzothiazolines at the same time.

In this chapter, the preparation of heterometallic d^{10} complexes of iminothiophenolate ligands derived from benzothiazolines is described. Two kinds of reaction procedures, (i) reactions of benzothiazolines with a mixture of two kinds of d^{10} metal ions ("one-pot" reaction) and (ii) reactions of two kinds of homometallic complexes ("metal-crossing" reaction), were carried out. The resulting heterometallic compounds were characterized by ^1H NMR and ESI mass spectra, fluorescent X-ray analysis, and single-crystals X-ray crystallography.

III-2. Experimental section.

III-2-1. General procedure.

Initial part of the reactions containing benzothiazolines were carried out using standard Schlenk techniques under an atmosphere of nitrogen, while other treatments and measurements were done in air.

III-2-2. Materials.

Benzothiazolines were prepared by the methods of the literature.[7] The starting materials [AuCl(tht)][8] (tht = tetrahydrothiophene), $[Cu(CH_3CN)_4]PF_6$, and $[Cu(CH_3CN)_4]ClO_4$[9] were prepared by the methods of the literature. The reagents were of the commercial grade and used without further purification.

III-2-3. Physical measurements.

The infrared spectra were measured with a JASCO FT/IR-4100 infrared spectrophotometer by using KBr pellet. The ^{1}H NMR spectra were recorded on a JEOL ECA-500 (500 MHz) and a JNM-GSX-400 (400 MHz) spectrometers, respectively, under a controlled temperature (30°C or 0°C) using tetramethylsilane (TMS) as internal standard (δ 0 ppm). The electronic absorption and diffusion reflectance spectra were recorded on a JASCO V-570 spectrophotometer. The elemental analyses (C, H, N) were performed at Osaka University. Electrospray ionization (ESI) mass spectra were recorded on a JASCO API LC-TOF/MS instrument. The fluorescence X-ray analyses were made on a HORIBA MESA-500 spectrometer. Single-crystal X-ray diffraction experiments were performed on a Rigaku RAXIS-RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation at 200 K. The intensity data were collected by the ω scan technique and were empirically corrected for absorption. The structures were solved by direct methods and were refined with full-matrix least-squares on F^2. Hydrogen atoms were placed at calculated positions but were not refined. All calculations were performed using Yadokari-XG 2009 software package,[10] except the refinements that were performed using SHELXL-97.[11]

III-2-4. Preparation of heterometallic complexes.

III-2-4-1. Preparation of Au^I-Ag^I complexes 13 and 14.

(a) Synthesis of $[Au_2Ag_2(L^1)_4]$ (13).

Method A: "one-pot" reaction.

To a yellow solution of 2-(4-dimethylaminophenyl)benzothiazoline (0.05 g, 0.20 mmol) in 15 mL of $CHCl_3$ were added Et_3N (0.02 g, 0.22 mmol) and [AuCl(tht)] (0.03 g, 0.10 mmol) in 2 mL of $CHCl_3$, followed by the addition of silver(I) perchlorate (0.02 g, 0.10 mmol) dissolved in 2 mL of EtOH. The slow evaporation of the solution at room temperature gave yellow crystalline powder of **13** after 3 days. Yield: 0.07 g, 71%. Anal. Found: C, 39.67; H, 3.27; N, 5.96%. Calcd for $[Au_2Ag_2(L^1)_4]\cdot 2CHCl_3$: C, 39.83; H, 3.34; N, 5.99%. ^1H NMR (500 MHz, $CDCl_3$, 30°C): δ 8.07 (1H, s, C*H*=N), 7.72 (1H, d, C*H* of N,S-Ph), 7.62 (2H, d, C*H* of pendant-Ph), 7.14 (1H, t, C*H* of N,S-Ph), 7.04 (1H, t, C*H* of N,S-Ph), 6.85 (1H, d, C*H* of N,S-Ph), 6.08 (2H, d, C*H* of pendant-Ph), 2.95 (6H, s, CH_3). Single crystals of **13** suitable for X-ray analysis were obtained directly from the reaction solution, when CH_2Cl_2 was used as a solvent instead of $CHCl_3$.

Method B: "metal-crossing" reaction.

To a yellow solution of $[Au_4(L^1)_4]\cdot CHCl_3$ (**1**) (0.03 g, 13 mmol) in 10 mL of $CHCl_3$ was added a yellow solution of $[Ag_4(L^1)_4]\cdot CHCl_3$ (**3**) (0.02 g, 13 mmol) in 10 mL of $CHCl_3$. The slow evaporation of the solution at room temperature gave yellow crystals of **13** after 3 days. Yield: 0.04 g, 78%. Anal. Found: C, 40.23; H, 3.31; N, 6.08%. Calcd for $[Au_2Ag_2(L^1)_4]\cdot 1.8CHCl_3$: C, 40.21; H, 3.37; N, 6.07%. ^1H NMR (500 MHz, $CDCl_3$, 30°C): δ 8.06 (1H, s, C*H*=N), 7.71 (1H, d, C*H* of N,S-Ph), 7.61 (2H, d, C*H* of pendant-Ph), 7.13 (1H, t, C*H* of N,S-Ph), 7.03 (1H, t, C*H* of N,S-Ph), 6.83 (1H, d, C*H* of N,S-Ph), 6.09 (2H, d, C*H* of pendant-Ph), 2.94 (6H, s, CH_3).

(b) Synthesis of $[Au_2Ag_2(L^2)_4]$ (14).

Method A: "one-pot" reaction.

To a yellow solution of 2-(2,4,6-trimethylphenyl)benzothiazoline (0.50 g, 1.96 mmol) in 20 mL of $CHCl_3$ were added Et_3N (0.10 g, 1.02 mmol) and [AuCl(tht)] (0.31 g, 0.98 mmol) in 5 mL of $CHCl_3$, followed by the addition of silver(I) acetate (0.16 g, 0.98 mmol). After filtration, the reaction solution was concentrated to a small volume, and 10 mL of n-C_6H_{14} was added to it. The resulting yellow powder of **14** was collected by filtration and washed with EtOH and n-C_6H_{14}. Yield: 0.71 g, 88%. Anal. Found: C, 47.02; H, 3.96; N, 3.61%. Calcd for $[Au_2Ag_2(L^2)_4]$: C, 47.24; H, 3.96; N, 3.44%. ^{1}H NMR (400 MHz, $CDCl_3$, 30C): δ 8.49 (1H, s, C*H*=N), 7.34 (1H, d, C*H* of N,S-Ph), 7.09 (1H, t, C*H* of N,S-Ph), 7.01 (1H, t, C*H* of N,S-Ph), 6.77 (1H, d, C*H* of N,S-Ph), 6.66 (2H, s, C*H* of pendant-Ph), 2.32 (3H, s, CH_3), 2.21 (6H, s, CH_3). Single crystals of **14** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into a $CHCl_3$ solution of **14**.

Method B: “metal-crossing” reaction.

To a yellow solution of $[Au_4(L^2)_4]$ (**2**) (0.02 g, 0.01 mmol) in 1 mL of $CHCl_3$ was added a yellow solution of $[Ag_4(L^2)_4]$ (**4**) (0.02 g, 0.01 mmol) in 1 mL of $CHCl_3$. The mixture was stirred at room temperature for 10 min, 10 mL of n-C_6H_{14} was added to it, and then concentrated to a small volume. The resulting yellow precipitate of **14** was collected by filtration and washed with EtOH. Yield: 0.03 g, 88%. Anal. Found: C, 47.61; H, 4.19; N, 3.33%. Calcd for $[Au_2Ag_2(L^2)_4]\cdot 0.2C_6H_{14}$: C, 47.62; H, 4.09; N, 3.41%. ^{1}H NMR (400 MHz, $CDCl_3$, 30°C): δ 8.49 (1H, s, C*H*=N), 7.34 (1H, d, C*H* of N,S-Ph), 7.09 (1H, t, C*H* of N,S-Ph), 7.01 (1H, t, C*H* of N,S-Ph), 6.76 (1H, d, C*H* of N,S-Ph), 6.65 (2H, s, C*H* of pendant-Ph), 2.32 (3H, s, CH_3), 2.21 (6H, s, CH_3).

III-2-4-2. Preparation of Au^I-Cu^I complexes 15 and 16.

(a) Synthesis of $[Au_2Cu_2(L^1)_4]$ (15).

Method A: “one-pot” reaction.

To a yellow solution of 2-(4-dimethylaminophenyl)benzothiazoline (0.05 g, 0.20 mmol) in 20 mL of $CHCl_3$ were added Et_3N (0.02 g, 0.22 mmol) and [AuCl(tht)] (0.03 g, 0.10 mmol) in 4 mL of $CHCl_3$, followed by the addition of $[Cu(CH_3CN)_4]PF_6$ (0.03 g, 0.10 mmol) dissolved in 4 mL of CH_3CN. The reaction mixture was stirred at room temperature for 2 min and slowly concentrated for 3 days to give orange crystals of **15** suitable for X-ray analysis. Yield: 0.05 g, 51%. Anal. Found: C, 41.75; H, 3.51; N, 6.41%. Calcd for $[Au_2Cu_2(L^1)_4]\cdot 2CHCl_3$: C, 41.81; H, 3.51; N, 6.29%. ^{1}H NMR (500 MHz, DMSO-d_6, 30°C): δ 8.13 (1H, s, C*H*=N), 7.66 (2H, d, C*H* of pendant-Ph), 7.57 (1H, d, C*H* of N,S-Ph), 7.05 (1H, t, C*H* of N,S-Ph), 6.97 (1H, t, C*H* of N,S-Ph), 6.92 (1H, d, C*H* of N,S-Ph), 6.01 (2H, d, C*H* of pendant-Ph), 2.85 (6H, s, C*H*$_3$).

(b) Synthesis of $[Au_2Cu_2(L^2)_4]$ (16).

Method A: "one-pot" reaction.

To a yellow solution of 2-(2,4,6-trimethylphenyl)benzothiazoline (0.50 g, 1.96 mmol) in 6 mL of $CHCl_3$ were added Et_3N (0.21 g, 2.06 mmol) and [AuCl(tht)] (0.31 g, 0.98 mmol) in 8 mL of $CHCl_3$, followed by the addition of a solution of $[Cu(CH_3CN)_4]PF_6$ (0.32 g, 0.98 mmol) in 20 mL of CH_3CN. The reaction solution was concentrated to a half volume. The resulting red-orange powder of **16** was collected by filtration and washed with CH_3CN. The filtrate were stood in a freezer for 1 day and then filtered to obtain orange crystals of **16**. Yield: 0.68 g, 90%. Anal. Found: C, 48.83; H, 4.09; N, 3.74%. Calcd for $[Au_2Cu_2(L^2)_4]\cdot 0.3CH_3CN\cdot 0.4CHCl_3$: C, 48.84; H, 4.12; N, 3.77%. ^{1}H NMR (500 MHz, $CDCl_3$, 30°C): δ 8.50 (1H, s, C*H*=N), 7.06-7.03 (2H, m, C*H* of N,S-Ph), 6.95 (1H, t, C*H* of N,S-Ph), 6.85 (1H, d, C*H* of N,S-Ph), 6.65 (2H, s, C*H* of pendant-Ph), 2.35 (3H, s, C*H*$_3$), 2.11 (6H, s, C*H*$_3$).

Method B: "metal-crossing" reaction.

To a yellow solution of $[Au_4(L^2)_4]$ **(2)** (0.02 g, 10 μmol) in 1 mL of $CHCl_3$ was added a yellow solution of $[Cu_3(L^2)_3]\cdot 0.5CHCl_3$ **(10)** (0.01 g, 14 μmol) in 1 mL of $CHCl_3$. The mixture was stirred at room temperature for 10 min, 20 mL of *n*-C_6H_{14} was added to it, and then concentrated to a small volume. The resulting orange precipitate of **16** was collected by filtration. Yield: 0.01 g, 45%. Anal. Found: C, 50.51; H, 4.32; N, 3.54%. Calcd for $[Au_2Cu_2(L^2)_4]\cdot 0.3C_6H_{14}$: C, 50.52; H, 4.39; N, 3.58%. ^{1}H NMR (500 MHz, $CDCl_3$, 30°C): δ 8.50 (1H, s, C*H*=N), 7.06-7.03 (2H, m, C*H* of N,S-Ph), 6.96 (1H, t, C*H* of N,S-Ph), 6.86 (1H, d, C*H* of N,S-Ph), 6.65 (2H, s, C*H* of pendant-Ph), 2.34 (3H, s, C*H*$_3$), 2.11 (6H, s, C*H*$_3$). Single crystals of **16** suitable for X-ray analysis were obtained by the recrystallization from *n*-C_5H_{12}.

III-2-4-3. Preparation of Ag^I-Cu^I complex 17.

Synthesis of $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl](ClO_4)_4$ (17).

Method A: "one-pot" reaction.

To a yellow solution of 2-(4-dimethylaminophenyl)benzothiazoline (0.17 g, 0.67 mmol) in 20 mL of 1,2-dichloroethane were added Et_3N (0.07 g, 0.69 mmol) and $[Cu(CH_3CN)_4]ClO_4$ (0.11 g, 0.33 mmol) in 6 mL of CH_3CN, followed by the addition of silver(I) perchlorate (0.07 g, 0.33 mmol) dissolved in 4 mL of 1,2-dichloroethane. The reaction mixture was stirred at room temperature for 5 min. A few single crystals of **17** suitable for X-ray analysis were obtained by the slow diffusion of n-C_5H_{12} into the dark brown reaction solution.

Method B: "metal-crossing" reaction.

To a yellow solution of $[Ag_4(L^1)_4]\cdot CHCl_3$ (**3**) (0.01 g, 7.3 μmol) in 3 mL of $CHCl_3$ was added a yellow solution of $[Cu_8(L^1)_8](PF_6)_2$ (**9**) (0.01 g, 3.6 μmol) in 3 mL of 1,2-dichloroethane. The reaction mixture was stirred at room temperature for 5 min. A few single crystals of **17** were obtained by the slow diffusion of n-C_5H_{12} into the dark brown reaction solution.

III-3. Results and discussion.

III-3-1. Reactions of a mixture of Au^I and Ag^I ions with benzothiazolines.

The 2:1:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with [AuCl(tht)] and silver(I) perchlorate under the presence of Et_3N gave a yellow solution, from which yellow powder of **13** was obtained in a high yield. An analogous reaction using 2-(2,4,6-trimethyphenyl)benzothiazoline instead of 2-(4-dimethylaminophenyl)benzothiazoline gave yellow powder of **14** in a high yield.

The fluorescence X-ray analysis indicated that **13** and **14** contain both Au and Ag atoms. The elemental analytical data of **13** and **14** were in agreement with formulas containing Au and Ag atoms, and iminothiophenolate ligands (L^1 and L^2) in a 1:1:2 ratio. The ^1H NMR spectra of **13** and **14** in $CDCl_3$ at 30°C showed singlet signals of azomethine protons appeared at δ 8.04 and 8.49 ppm, respectively (Figure 3-1). Therefore, it is suggested that the starting benzothiazolines converted to the iminothiolate ligand (L^1 and L^2) by complexation. Moreover, the appearance of a single set of signals in the ^1H NMR spectra showed that there is only one environment of ligand (L^1 and L^2) in each of complex **13** and **14**. The ESI mass spectrum of **13** in CH_2Cl_2/MeOH (1:1) showed a weak signal corresponding to $[Au_2Ag_2(L^1)_4]+H^+$ (m/z = 1631.1) and a relatively strong signal corresponding to $[Au_2Ag_2(L^1)_4]+Ag^+$ (m/z = 1739.0) (Figure 3-2). Considering these results, it is suggested that single and high symmetrical heterometallic tetranuclear complexes $[Au_2Ag_2(L^1)_4]$ and $[Au_2Ag_2(L^2)_4]$ were exclusively obtained from the reactions of benzothiazolines with two kinds of metal ions (Au^I and Ag^I).

Single crystals of **13** and **14** suitable for X-ray analysis were prepared by the slow diffusion of n-C_5H_{12} into the yellow reaction solutions. The crystallographic data of **13** and **14** are summarized in Table 3-1. The selected bond distances and angles of **13** and **14** are summarized in Tables 3-2 and 3-3. Single-crystal X-ray analysis revealed that **13** has a tetranuclear metalloring structure, $[Au_2Ag_2(L^1)_4]$, consisting of two Au^I and two Ag^I atoms bridged by four S atoms from four L^1 ligands, as expected (Figure 3-3(a)). In **13**, Au^I and Ag^I atoms are alternately arranged and adopt S_2 linear and distorted N_2S_2 tetrahedral geometries, respectively. The metalloring structure of **13** is very similar to that of $[Ag_4(L^1)_4]$ (**3**), but two-coordinated Ag^I atoms in **3** are replaced by Au^I atoms in **13**. The absolute configurations of four sulfur atoms in **13** are *S*, *S*, *R*, and *R*. The bond distances and angles of each tetrahedral Ag^I atom in **13** (av. Ag–S = 2.462(2) Å, av. Ag–N = 2.611(6) Å, S–Ag–S = 137.42(6)°) are comparable with those in **3**, and the bond distances and angles about each Au^I atom in **13** (av. Au–S = 2.299(2) Å, S–Au–S = 175.86(6)°) are essentially the same as those in $[Au_4(L^1)_4]$ (**1**). The structure of **14** was reminiscent of that of **13** (Figure 3-3 (b)). The M–S distances and S–M–S angles of **14** are very similar to those of **13**, while the Ag1···N1 distance in **14** (3.596(7) Å) is longer than that in **13** (2.677(5) Å) because of the steric constraint of methyl group in **14**.

It is possible that three heterometallic species, $[Au_3Ag_1L_4]$, $[Au_2Ag_2L_4]$, and $[Au_1Ag_3L_4]$, besides two homometallic species, $[Au_4L_4]$ and $[Ag_4L_4]$, are formed from L in combination with Au^I and Ag^I (Chart 3-1). In addition, two isomeric forms that are discriminated by the arrangement of Au^I and Ag^I atoms, AuAuAgAg-type and AuAgAuAg-type, are possible even when $[Au_2Ag_2L_4]$ is exclusively formed. However, the ^1H NMR spectrum of reaction mixtures of 2-(4-dimethylaminophenyl)benzothiazoline, [AuCl(tht)], and silver(I) perchlorate in a 2:1:1 ratio in $CDCl_3$ exhibited dominantly a single set of proton signals that are identical with the signals for **13** (Figure 3-4), indicative of the selective formation of $[Au_2Ag_2(L^1)_4]$ with an AuAgAuAg-type arrangement because if AuAuAgAg arrangement, three sets signals of L^1 should be observed. In these compounds **13** and **14**, each L ligand adopts a μ_2-κ^1S:κ^2N,S coordination mode, rather than a μ_2-κ^1S:κ^1S mode with a free imine group, and furthermore, the two-coordinate metal sites are occupied by Au^I atoms that form stronger bonds with thiolate groups compared with Ag^I atoms. These two structural factors, which appear to contribute significantly to the thermodynamic stability, are not satisfied together in the other possible metalloring species and isomers and thus might account for the selective formation of **13** and **14**.

To sum up the Au^I-Ag^I system, the treatments of benzothiazolines with Au^I and Ag^I ions selectively afforded the heterometallic tetranuclear metallorings $[Au_2Ag_2L_4]$ (L = L^1 (**13**), L^2 (**14**)) with alternate metal arrangement (Scheme 3-1). The selective coordination of imine groups to Ag^I centers, together with the S_2 linear coordination geometry of Au^I centers, is a key factor of these exclusive and regioselective heterometallic reactions.

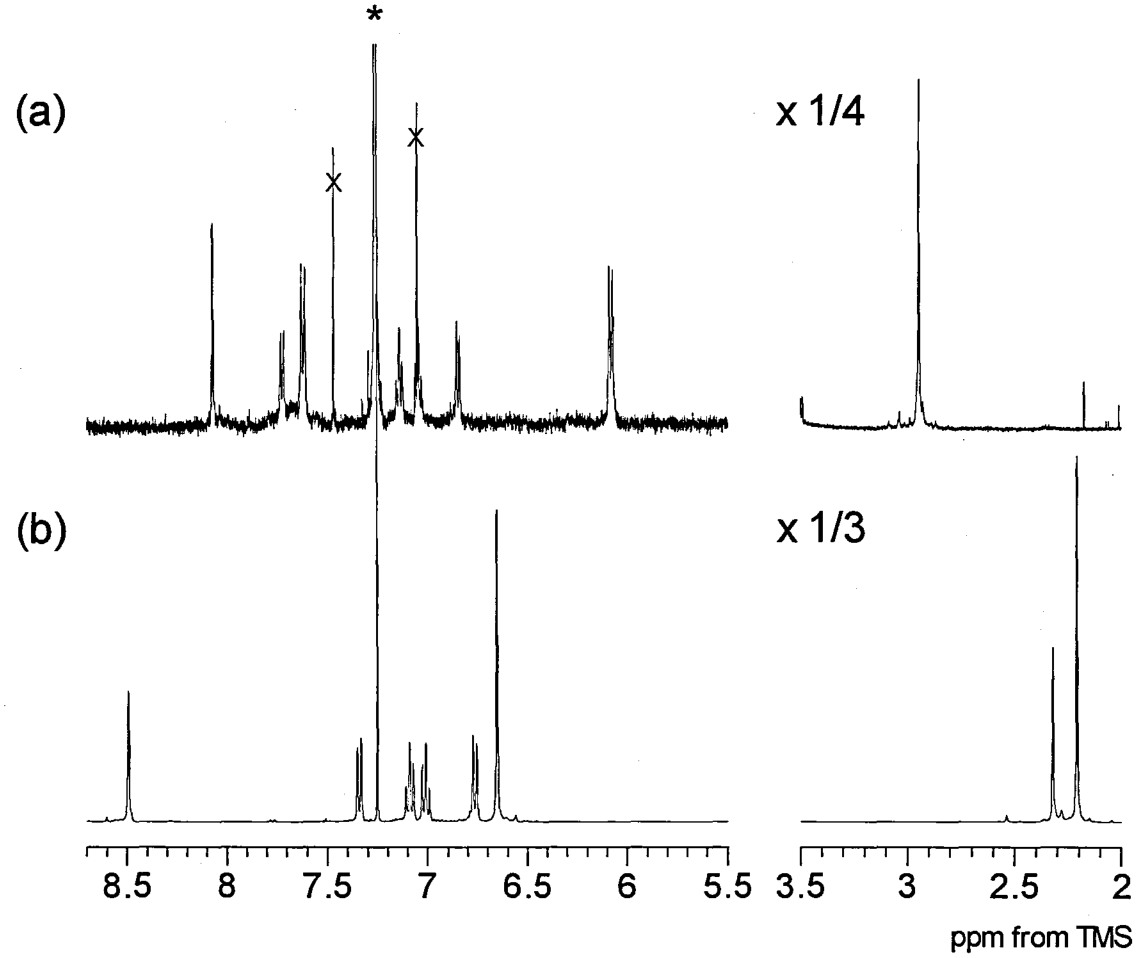


Figure 3-1. ^{1}H NMR spectra of (a) **13** and (b) **14** in $CDCl_3$ at 30°C. (*) denotes a signal of solvent.

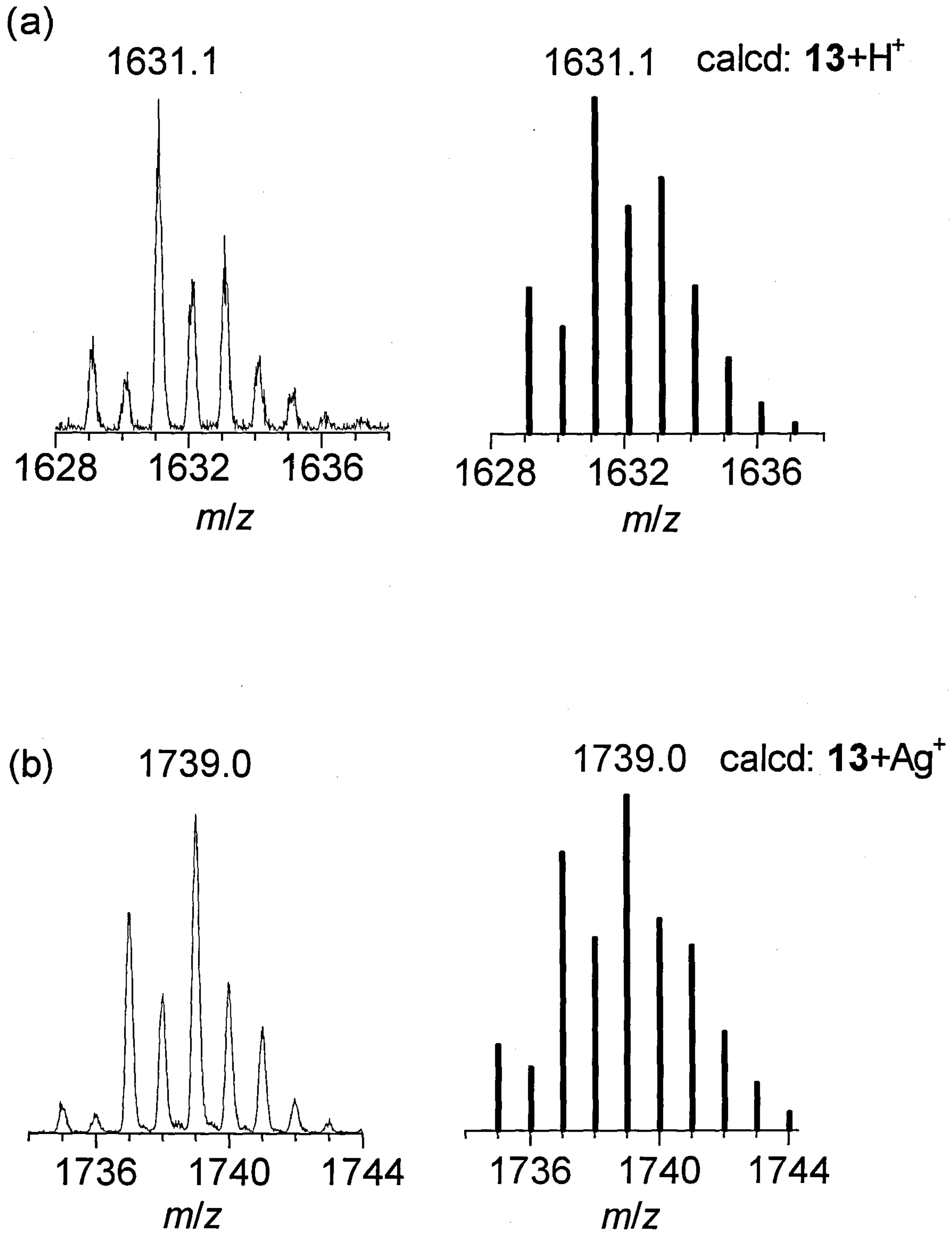


Figure 3-2. ESI mass spectra of **13** in CH_2Cl_2/MeOH (1:1). Observed signal at (a) *m*/*z* = 1631.1 (left) together with the calculated pattern for **13**+H^+ (right) and (b) *m*/*z* = 1739.0 (left) together with the calculated pattern for **13**+Ag^+ (right).

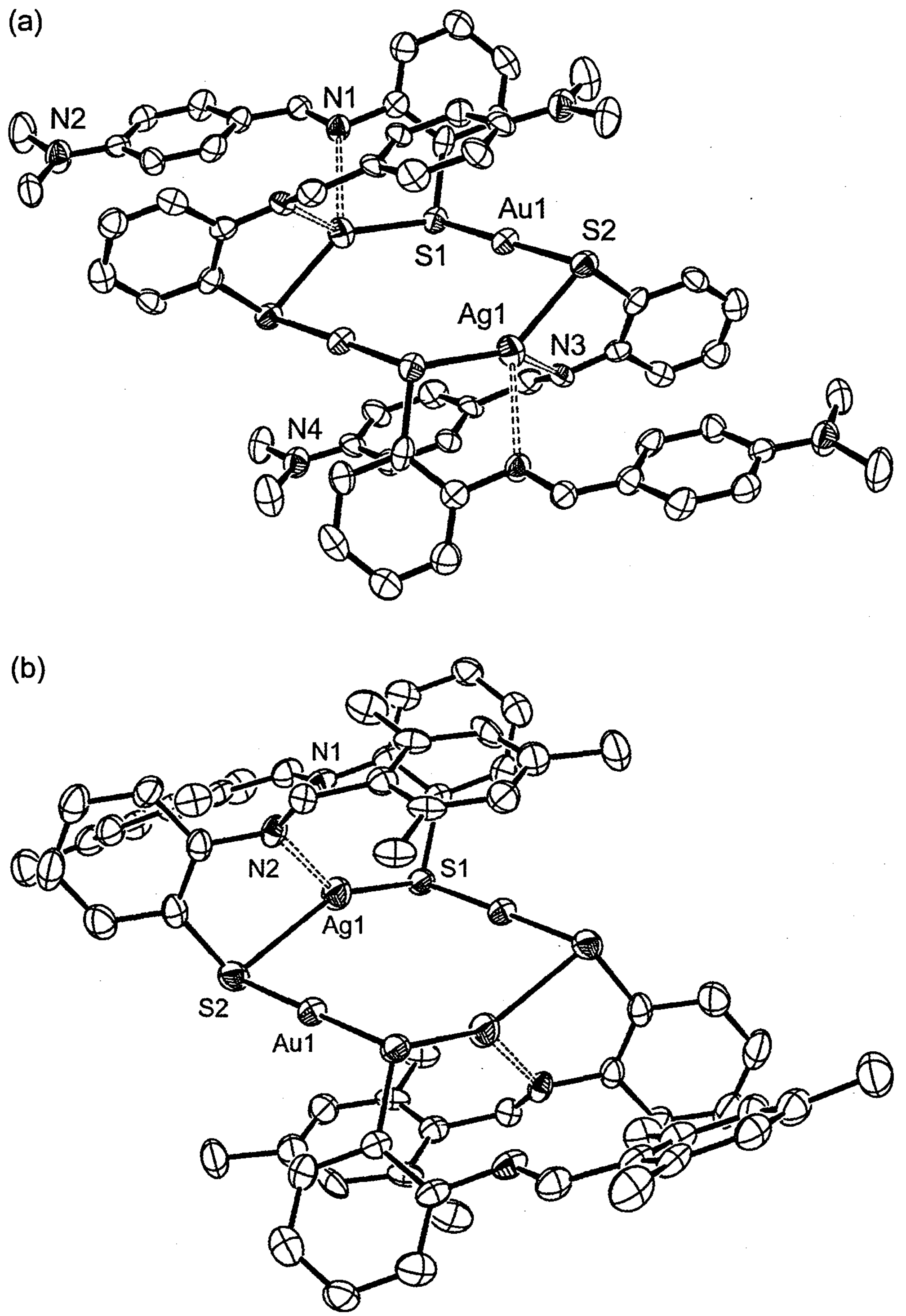


Figure 3-3. Perspective views of (a) **13** and (b) **14**. Hydrogen atoms are omitted for clarity.

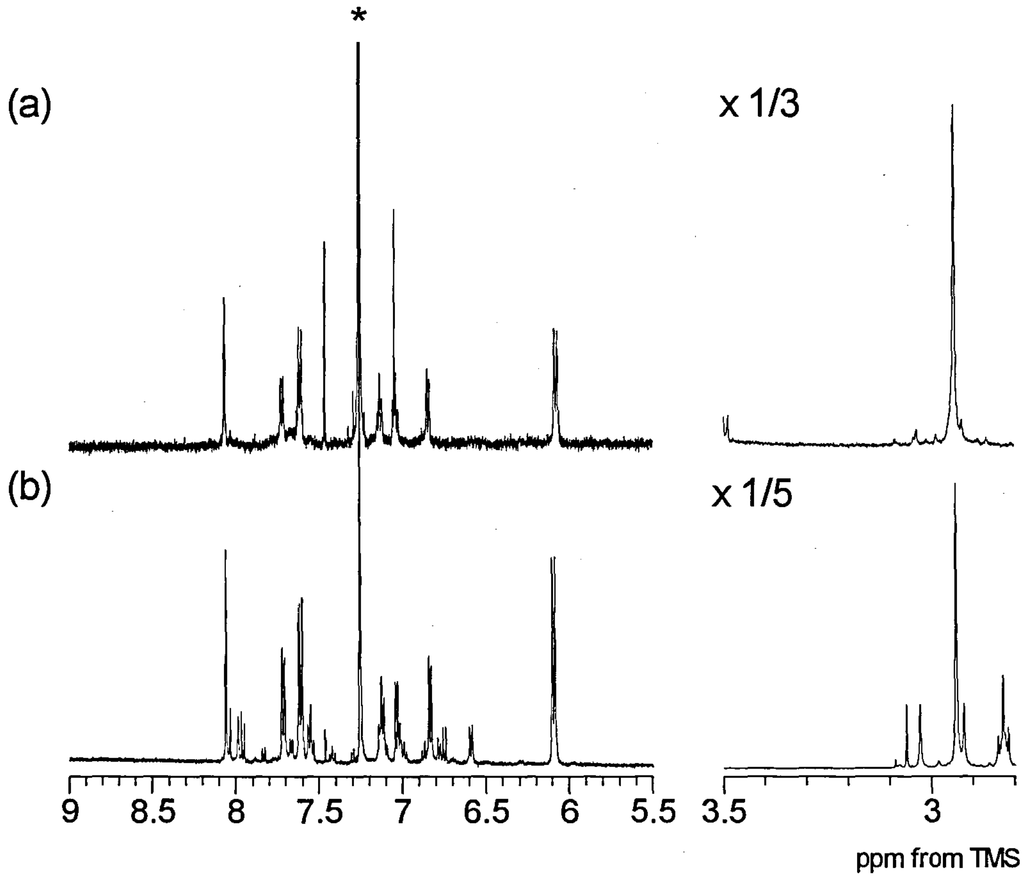


Figure 3-4. ^{1}H NMR spectra of (a) **13** and (b) a 1:1:2 mixture of Au^I, Ag^I, and 2-(4-dimethylaminophenyl)benzothiazoline in CDCl$_3$ at 30°C. (*) denotes a signal of solvent.

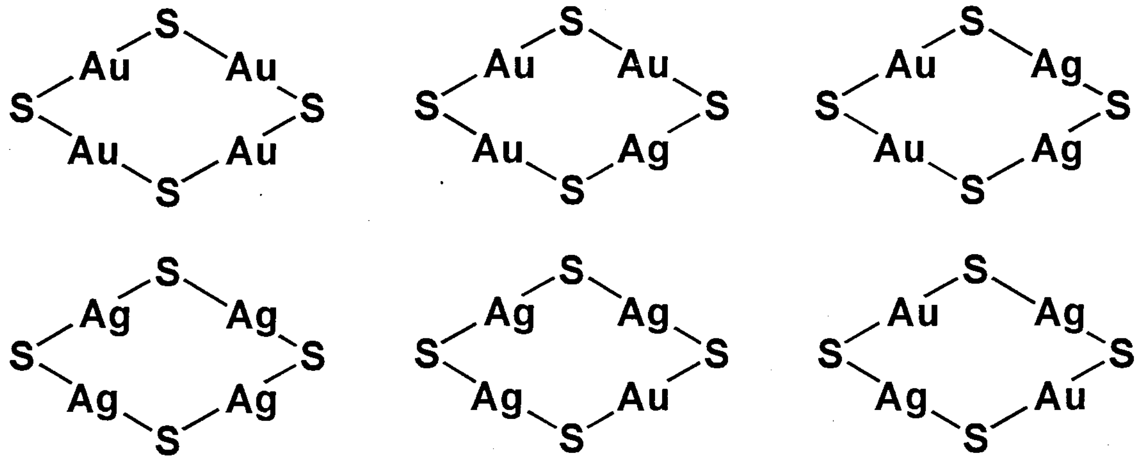
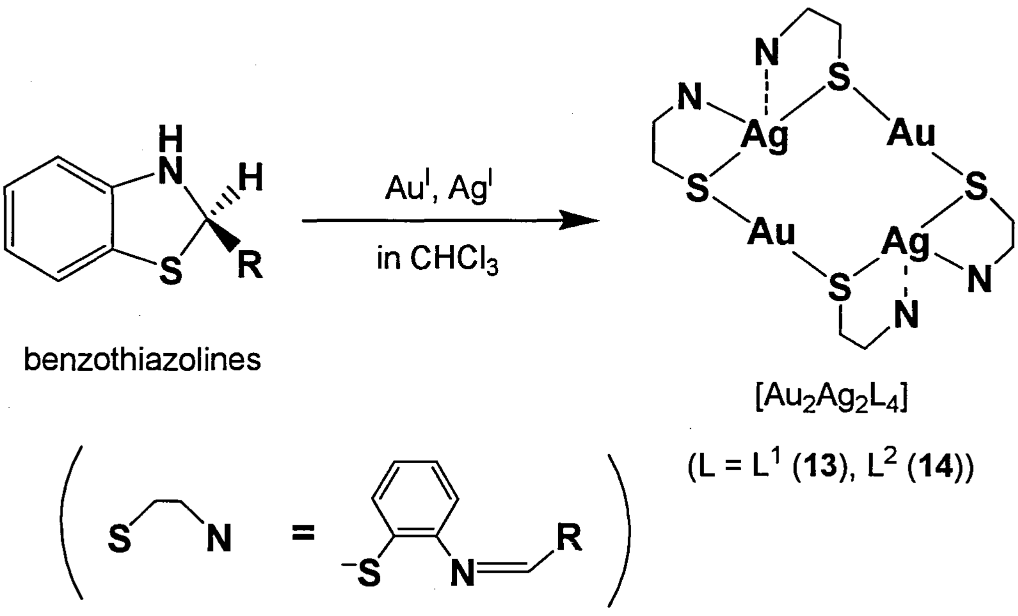


Chart 3-1. Possible Structures of S-bridged tetranuclear rings {Au^I_mAg^I_nS$_4$} (m+n = 4).



Scheme 3-1. Reactions of benzothiazolines with a mixture of Au^I and Ag^I ion.

III-3-2. Reactions of a mixture of Au^I and Cu^I ions with benzothiazolines.

The 2:1:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with [AuCl(tht)] and $[Cu(CH_3CN)_4]PF_6$ under the presence of Et_3N in $CH_3CN/CHCl_3$ at room temperature gave an orange solution, from which yellow crystals of **15** were obtained in a moderate yield. An analogous reaction using 2-(2,4,6-trimethyphenyl)benzothiazoline instead of 2-(4-dimethylaminophenyl)benzothiazoline gave yellow powder of **16** in a high yield.

The fluorescence X-ray analysis indicated that **15** and **16** contain both Au and Cu atoms. The elemental analytical data of **15** and **16** were in agreement with formulas containing Au and Cu atoms, and iminothiophenolate ligands L in a 1:1:2 ratio. As found in the $Au^I_2Ag^I_2$ complexes **13** and **14**, the ^{1}H NMR spectra of **15** in DMSO-d_6 and **16** in $CDCl_3$ at 30°C showed singlet signals of azomethine protons appeared at δ 8.13 and 8.50 ppm, respectively (Figure 3-5). Therefore, it is suggested that the starting benzothiazolines converted to the iminothiolate ligand (L^1 and L^2) by complexation. Considering these results, it was suggested that **15** and **16** are heterometallic tetranuclear metallorings $[Au_2Cu_2L_4]$, in which two Ag^I ions of $[Au_2Ag_2L_4]$ are replaced by two Cu^I ions.

Single crystals of **15** were prepared by the slow diffusion of n-C_5H_{12} into the yellow reaction solution, while single crystals of **16** were obtained from other reaction procedure, "metal-crossing" reaction (see Chapter III-4). The crystallographic data are summarized in Table 3-1. The selected bond distances and angles are summarized in Tables 3-4 and 3-5. Single-crystal X-ray analysis revealed that **15** has a tetranuclear metalloring structure in $[Au_2Cu_2(L^1)_4]$ consisting of two Au^I and two Cu^I ions bridged by four S atoms of four L^1 ligands (Figure 3-6 (a)). In **15**, Au^I and Cu^I atoms are alternately arranged and adopt S_2 linear and distorted N_2S_2 tetrahedral geometries, respectively. The absolute configuration of four sulfur atoms in **15** are *S*, *S*, *R*, and *R*, respectively. These structural features of **15** are very similar to those of **13**, except for two Cu^I ions which are displaced by Ag^I ions in **13**. The Au–S lengths and S–Au–S angles of **15** are similar to those of $[Au_4(L^1)_4]$ (**1**), while the Cu–S and Cu–N lengths of **15** are similar to those of the tetrahedral Cu^I ions in $[Cu_4(L^4)_4]$ (**11**). However, the S–Cu–S angle (111.10(5)°) in **15** is smaller than that of the tetrahedral Cu^I ions in **11**

(133.22(3)°). A similar tetranuclear copper(I) metalloring, [Cu_4(2,2'-bipyridine)$_2${*S*(2,4,6-*i*$Pr_3C_6H_2$)}$_4$], in which two of four Cu^I atoms are situated in a distorted tetrahedral geometry coordinated by two 2,2'-bipyridine N and two thiolate S atoms and the others are in a digonal geometry coordinated by two thiolate S atoms, have been reported.[12]

Single-crystal X-ray analysis revealed that **16** is a tetranuclear metalloring, [$Au_2Cu_2(L^2)_4$], in which two Au^I and two Cu^I ions are bridged by four S atoms of four L^2 ligands (Figure 3-7 (a)). In **16**, Au^I and Cu^I atoms are alternately arranged and adopt S_2 linear and distorted N_2S_2 tetrahedral geometries, respectively. On the other hand, the metalloring structure has a molecular D_2 symmetry and the absolute configurations of four sulfur atoms in **16** are different from that of **15**, which exist both *R*, *R*, *R*, and *R* and *S*, *S*, *S*, and *S* in the crystal structure (Figure 3-7 (b)). Therefore, the metalloring structure of **16** is very different from other tetranuclear metallorings demonstrated above, although the bond lengths and angles of **16** are similar to those of **15** except for S–Cu–S angle (141.99(7)° for **16** and 111.10(5)° for **15**). The dihedral angle between two S–Au–S linear units is close to 90° in **16**, while that of **15** is almost 0° (Figure 3-6 (b)). In the crystal packing, each of *R*,*R*,*R*,*R* and *S*,*S*,*S*,*S* isomers arranged in a 2D fashion, and the two kinds of layers were piled up in an ABAB staking mode (Figure 3-8).

In short, it was found that the reaction of benzothiazoline with a mixture of Au^I and Cu^I ions lead to the regioselective formation of the $Au^I_2Cu^I_2$ heterometallic ring as found in the case of the heterometallic Au^I-Ag^I system (Scheme 3-2).

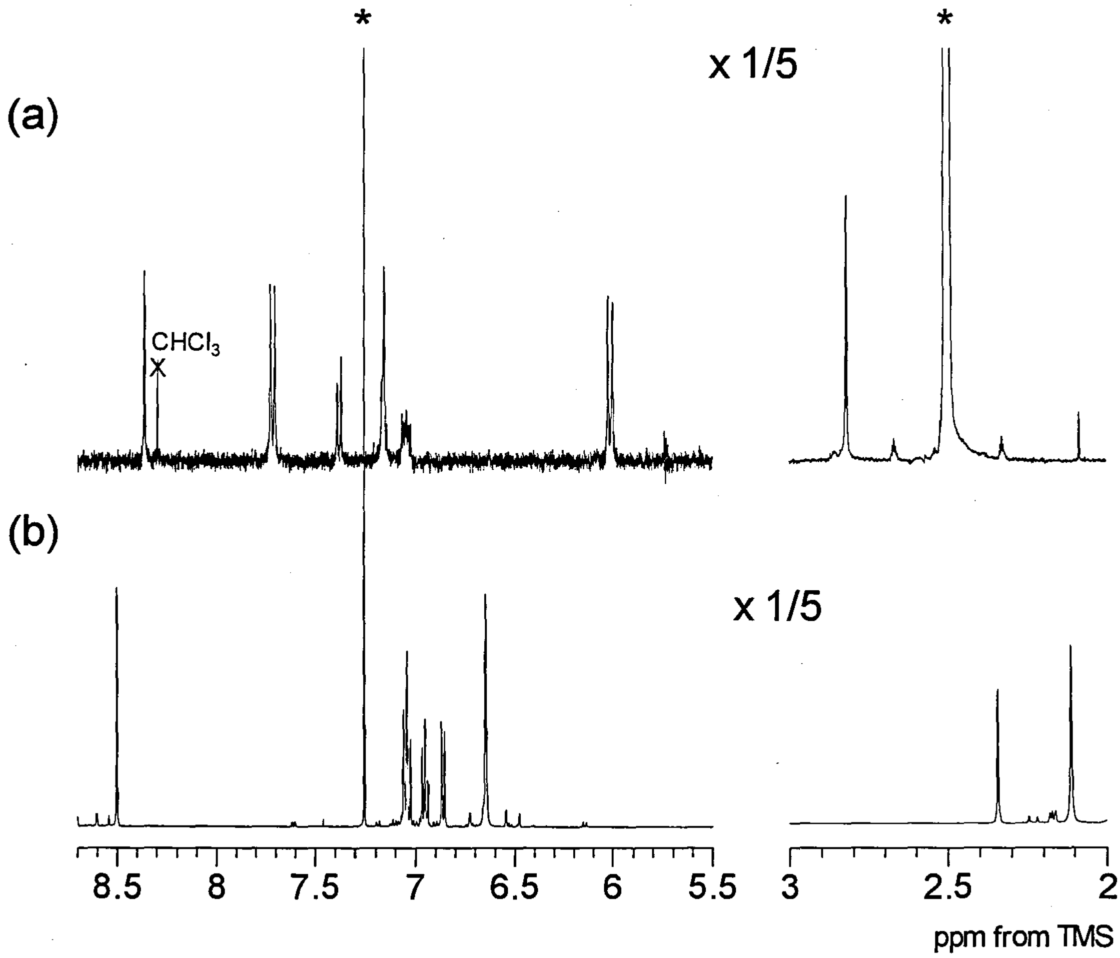


Figure 3-5. ^{1}H NMR spectra of (a) **15** in DMSO-d_6 and (b) **16** in $CDCl_3$ at 30°C. (*) denotes a signal of solvent.

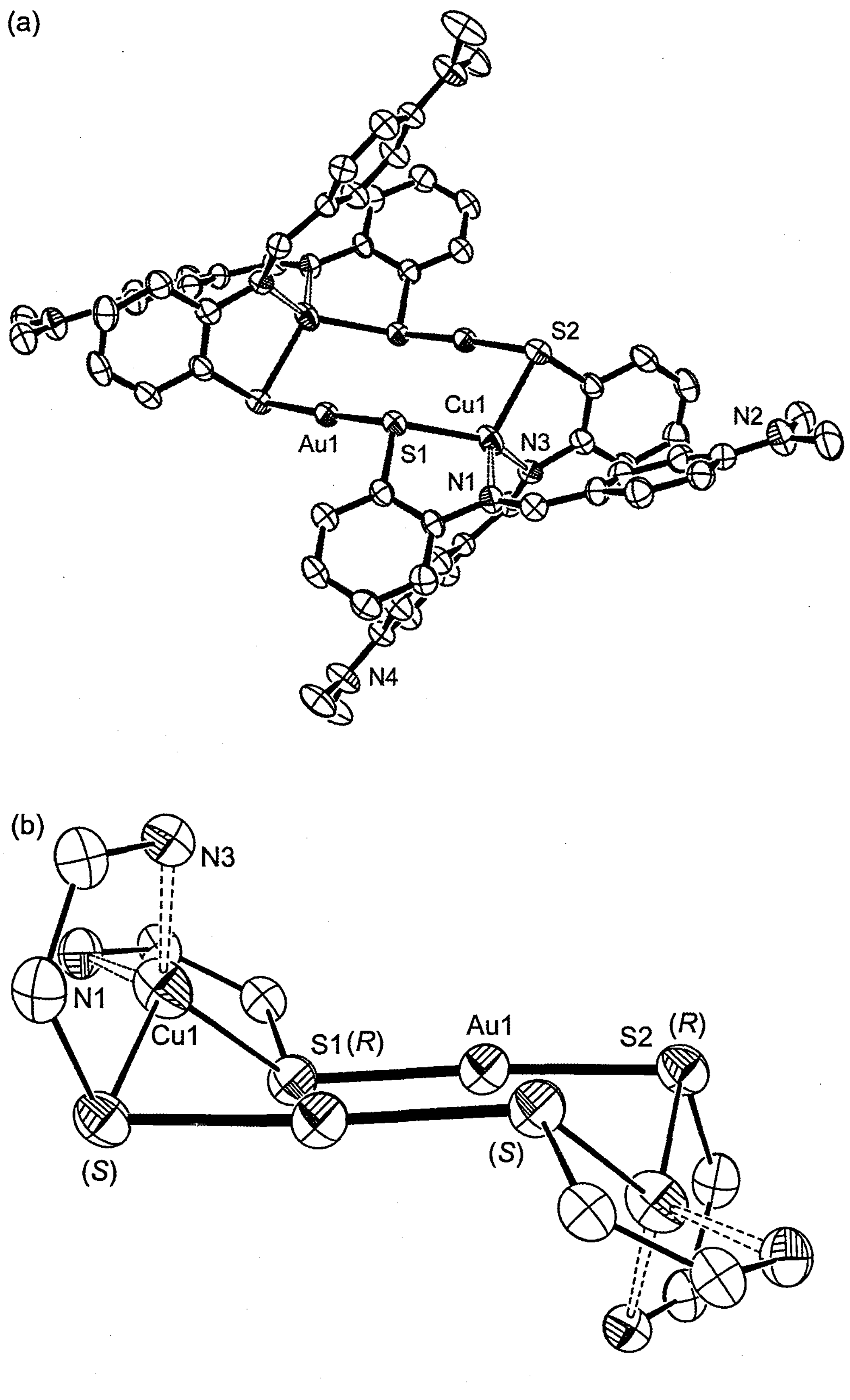


Figure 3-6. Perspective views of **15**. (a) Whole structure and (b) core structure. Hydrogen atoms are omitted for clarity.

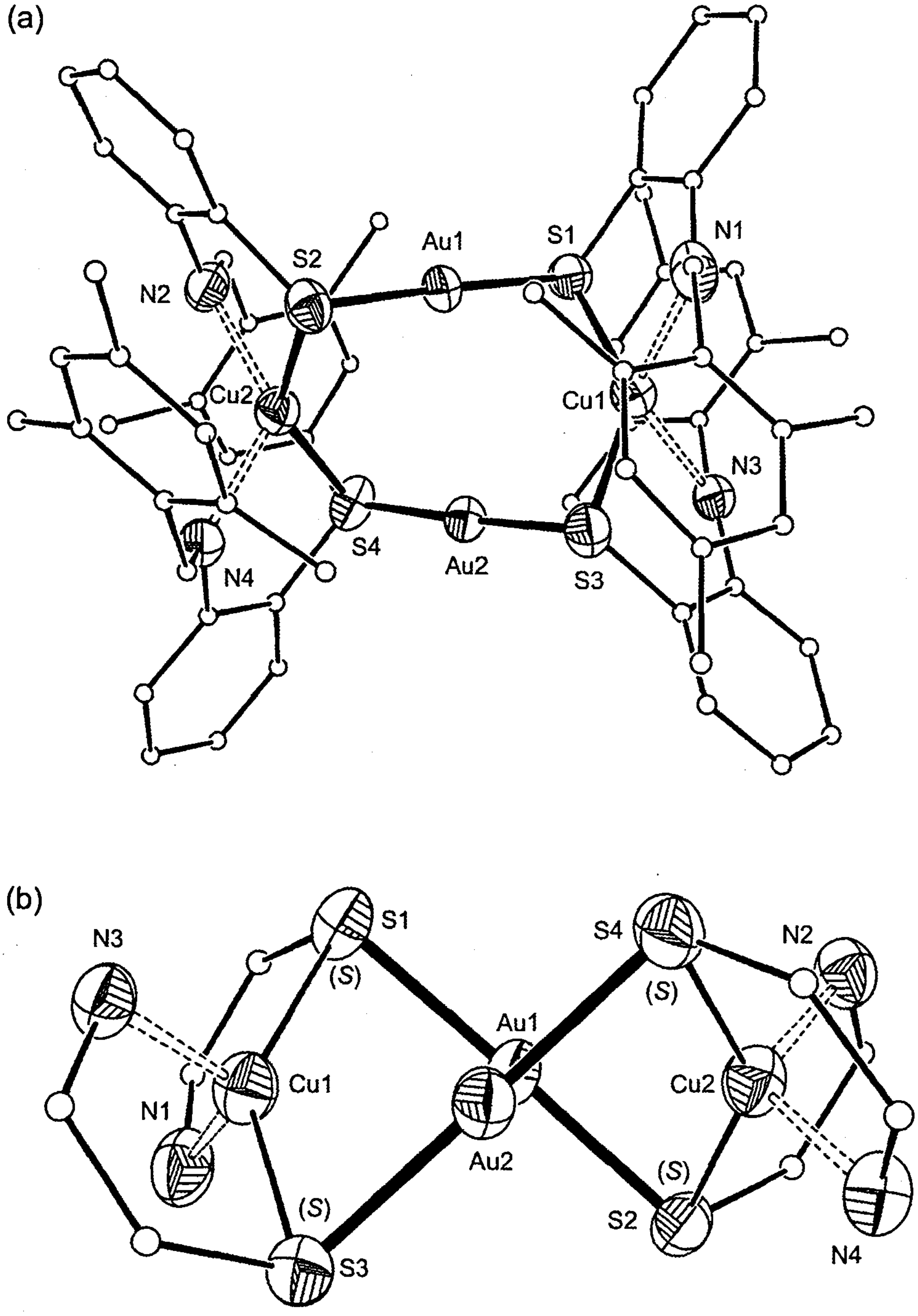


Figure 3-7. Perspective views of **16**. (a) Whole structure and (b) core structure. Hydrogen atoms are omitted for clarity.

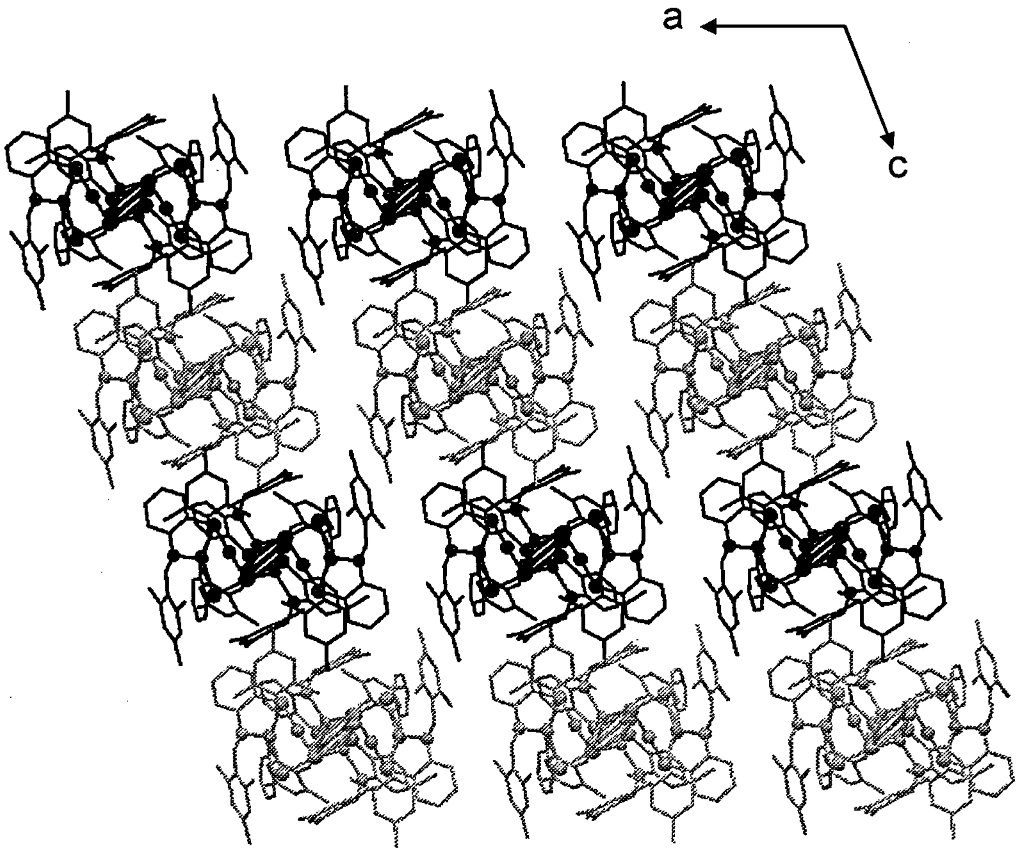
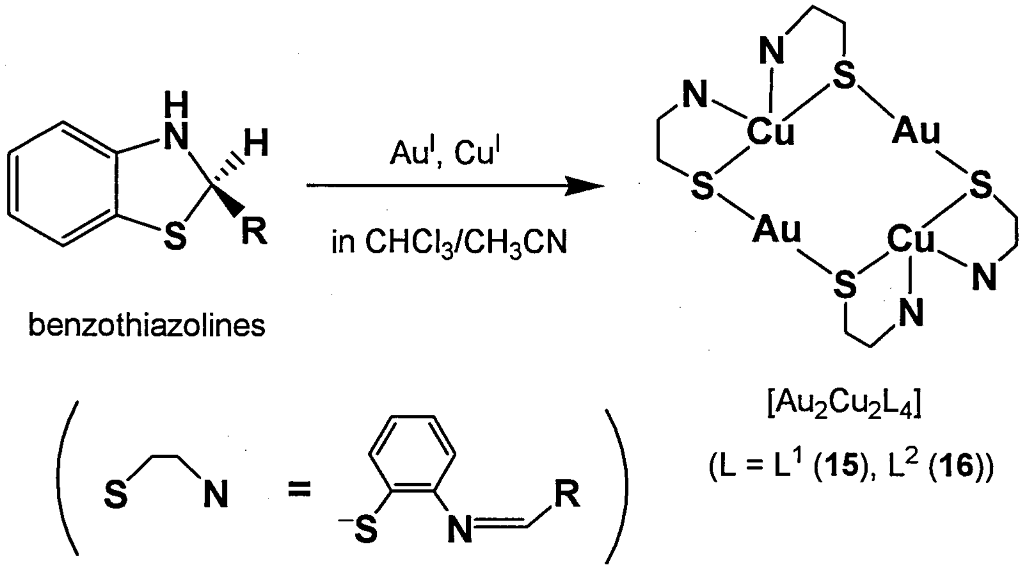


Figure 3-8. Packing structure of **16**. Black units are *S,S,S,S* species and gray units are *R,R,R,R* ones.



Scheme 3-2. Reactions of benzothiazolines with Au^I and Cu^I ion.

III-3-3. Reactions of a mixture of Ag^I and Cu^I ions with benzothiazolines.

The 2:1:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with Ag^I and Cu^I ions gave a yellow solution, from which an extremely small amount of red crystals of **17** suitable for X-ray analysis was obtained by vapor diffusion of n-C_5H_{12}.

The crystallographic data are summarized in Table 3-1. The selected bond distances and angles are summarized in Table 3-6. Single-crystal X-ray analysis revealed that **17** is a 21-nuclear campanulate-shape cluster, $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl](ClO_4)_4$. The asymmetric unit of **17** contains a half of cluster cation, $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl]$, and two perchlorate anions. The cluster-cation consists of twelve Ag^I ions, nine Cu^I ions, sixteen L^1 ligands, one Cl^- ion, besides one disordered CH_3CN (Figure 3-9). Considering the total charge of the complex-cation and the monoanionic nature of the iminothiolate ligand, each Ag and Cu atoms in **17** is assigned to have a +1 oxidation state. In **17**, there is a crystallographical C_2 axis through the central Cl1 and Cu1 coordinated by disordered CH_3CN. The metal ions and iminothiolate ligands adopt a lot of coordination environments and coordination modes, reflecting to the flexibility of coordination geometry in Ag^I and Cu^I ions. For twelve Ag^I ions, there are two S_2 linear (av. Ag–S = 2.43 Å), two NS_2 trigonal-planar (av. Ag–S = 2.58 Å, Ag–N = 2.28 Å), two NS_3 tetrahedral (av. Ag–S = 2.57 Å, Ag–N = 2.35 Å), two S_4 tetrahedral (av. Ag–S = 2.61 Å), and four S_3Cl trigonal-pyramidal (av. Ag–S = 2.59 Å, av. Ag–Cl = 2.79 Å) coordination environments (Chart 3-2). For nine Cu^I ions, there are one NS_2 trigonal-planar (Cu–S = 2.31 Å, Cu–N = 2.27 Å), two N_2S trigonal-planar (Cu–S = 2.25 Å, av. Cu–N = 2.01 Å), four NS_3 tetrahedral (av. Cu–S = 2.44 Å, av. Cu–N = 2.00 Å), and two N_2S_2 tetrahedral (av. Cu–S = 2.29 Å, av. Cu–N = 2.10 Å) coordination environments (Chart 3-3). On the other hand, in L^1 ligand, there are six types of coordination mode as shown in Chart 3-4.

The $\{Ag^I_{12}Cu^I_9S_{16}\}$ core that accommodates a Cl^- ion is covered by an organic layer like to the spherical 16-nuclear cluster $[Cu_{16}(L^1)_{12}Cl](PF_6)_3$ (**12-Cl**). Note that there exist six sets of intramolecular π-π interaction not only between *N*,*S*-bridging phenyl rings and pendent phenyl rings as found in **12-Cl** (face-to-tale type) but also face-to-face type in the organic layer. Two ligands located at bottom part adopt the unusual *N*,*S*-bridging mode similar to those in **12-X**.

In short, it was found that the reaction of benzothiazoline with a mixture of Ag^I and Cu^I ions lead to an unidentified mixture because of the flexible coordination geometry of both ions. However, it was found that one of the product is unexpected $Ag^I_{12}Cu^I_9$ 21-nuclear cluster, $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl](ClO_4)_4$ (**17**).

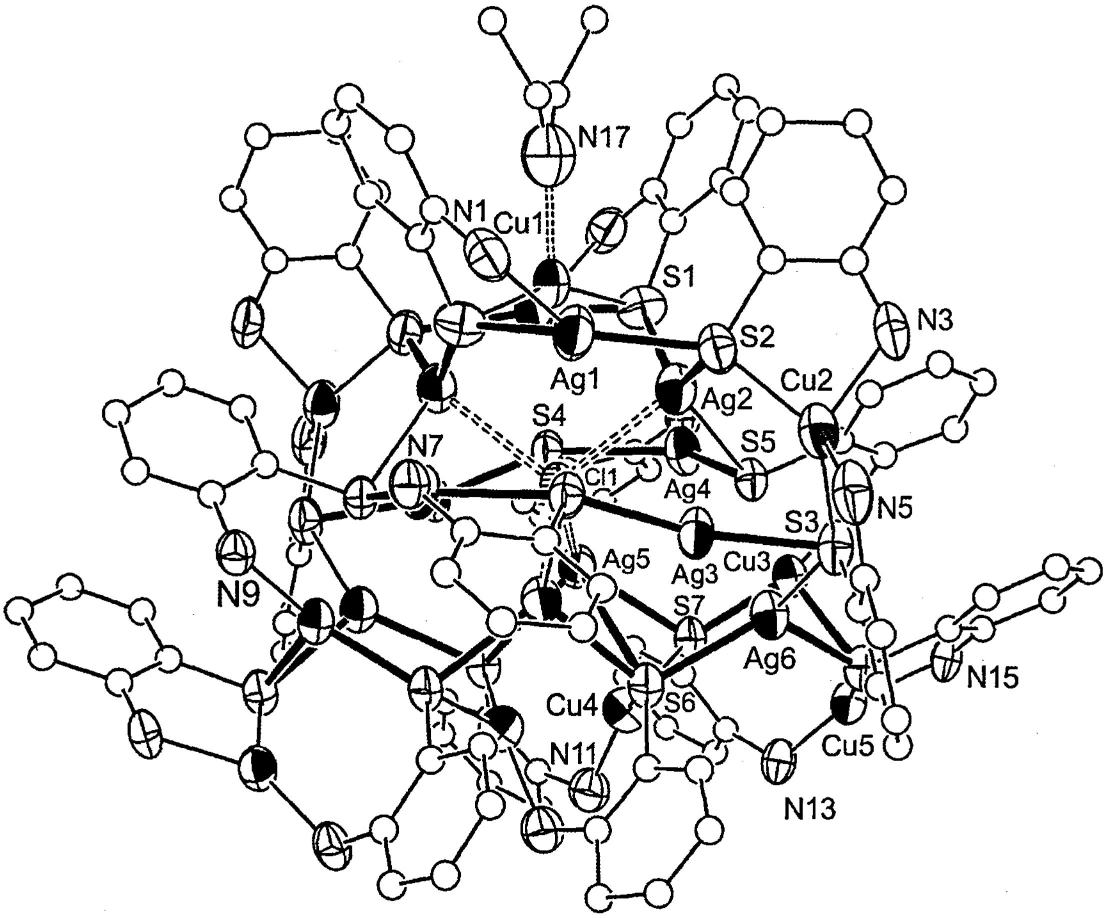


Figure 3-9. A perspective view of **17**. Hydrogen, imino-C, and pendant group are omitted for clarity.

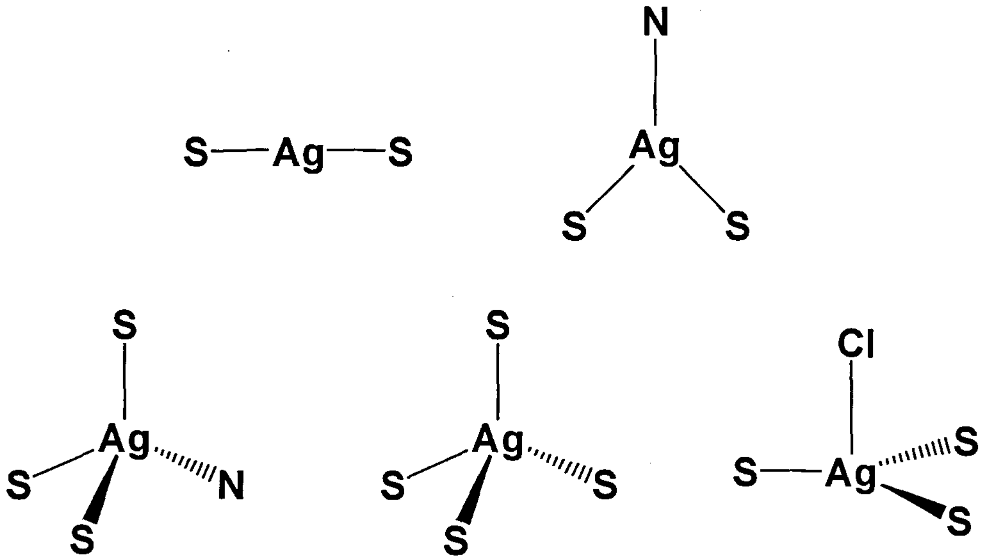


Chart 3-2. Coordination environments of Ag^I ion found in **17**.

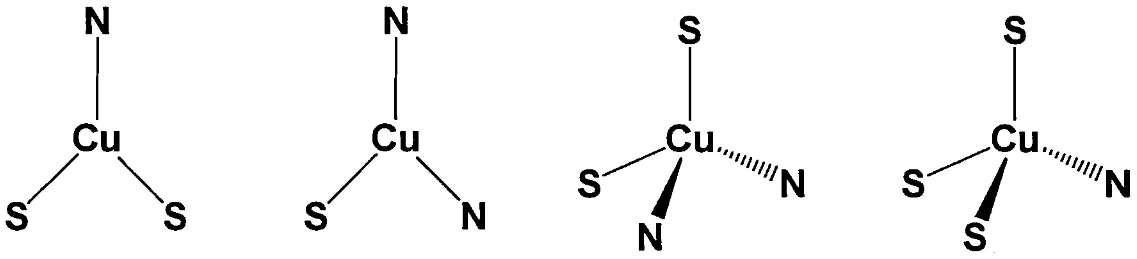


Chart 3-3. Coordination environments of Cu^{I} ion found in 17.

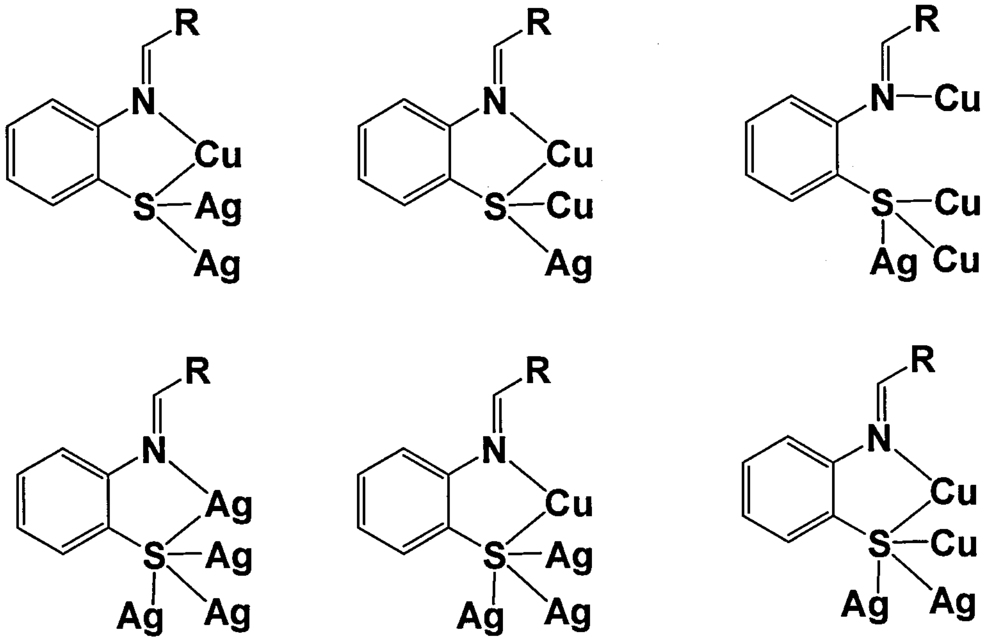


Chart 3-4. Coordination modes of L^{1} ligand found in 17.

III-3-4. "Metal-crossing" reactions with homometallic metallorings.

As shown in chapter III-3-1, the reactions of benzothiazolines with Au^I and Ag^I ions induced the selective formation of heterometallic tetranuclear complexes [$Au_2Ag_2L_4$] with an excellent regioselectivity. Therefore, it is expected that the Au^I-Ag^I heterometallic complex is formed by mixing the homometallic complexes [$Au_4(L^1)_4$] (**1**) and [$Ag_4(L^1)_4$] (**3**). The ^{1}H NMR spectrum of the mixture of **1** and **3** in $CDCl_3$ in a 1:1 ratio exhibited only a single set of signals corresponding to [$Au_2Ag_2(L^1)_4$] (**13**), while signals of **1** and **3** completely disappeared immediately (Figure 3-10). Therefore, it was found that the mixing reaction progressed quantitatively. Consistent with this observation, **13** was isolated in a good yield from a $CHCl_3$ solution containing **1** and **3** in a 1:1 ratio. As far as we know, such regioselective metal-exchange reaction between two metallorings with different metal ions has never been reported. Therefore, we call this phenomenon "metal-crossing" reaction (Scheme 3-3). Furthermore, a similar reaction between **2** and **4** gave [$Au_2Ag_2(L^1)_4$] (**14**), which was confirmed by ^{1}H NMR analysis in $CDCl_3$ (Figure 3-11).

To expand these "metal-crossing" reactions to other systems, the similar reaction was carried out in the Au^I-Cu^I system. The ^{1}H NMR spectrum of the reaction mixture of [$Au_4(L^1)_4$] (**1**) and [$Cu_8(L^1)_8$]$(PF_6)_2$ (**9**) in DMSO-d_6 in a 2:1 ratio showed only the signals of starting materials **1** and **9** just after dissolved at room temperature. However, after heating at 50 °C for 2 h, the ^{1}H NMR spectrum exhibited only new single set of signals corresponding to [$Au_2Cu_2(L^1)_4$] (**15**), which clearly demonstrated the progress of the "metal-crossing" reaction (Figure 3-12). In addition, the ^{1}H NMR spectra of the 3:4 mixture of [$Au_4(L^2)_4$] (**2**) and [$Cu_3(L^2)_3$]$^{2+}$ (**10**) in $CDCl_3$ showed the signals of the heterometallic compound [$Au_2Cu_2(L^2)_4$] (**16**) (Figure 3-13). Therefore, it was confirmed that the "metal-crossing" reaction occurs in the Au^I-Cu^I system.

However, when [$Ag_4(L^1)_4$] (**3**) and [$Cu_8(L^1)_8$]$^{2+}$ (**9**) were dissolved in DMSO-d_6 in a 2:1 ratio, its ^{1}H NMR spectrum showed the broadened signals, suggestive of the formation of a mixture. Furthermore, the 3:4 mixture of [$Ag_4(L^2)_4$] (**4**) and [$Cu_3(L^2)_3$]$^{2+}$ (**10**) in $CDCl_3$ also showed complicated and broadened signals in its ^{1}H NMR spectrum. These results showed that the "metal-crossing" reaction may not occur in the Ag^I-Cu^I system, though the structures of **4** and **10** were not retained.

However, an extremely small amount of $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl]^{4+}$ (**17**) was isolated by slow diffusion of n-C_5H_{12} into the mixture of **3** and **9** in $CHCl_3/CH_2ClCH_2Cl$, which was also obtained from the "one-pot" reaction of 2-(4-dimethylaminophenyl)benzothiazoline with Ag^I and Cu^I ions.

In short, it was found that the heterometallic metallorings were successfully constructed through the "metal-crossing" reaction of two homometallic metallorings with different metal ions. This reaction occurred only when Au^I metallorings having free imino groups were used. A detailed mechanism of this reaction is not clear at present, but it is most likely that the coordination of a free imine group in Au^I complex to a two-coordinate Ag^I center in Ag^I complex, followed by the coordination of its thiolato group, is a driving force of the selective formation of the heterometallic metalloring. The selective coordination of imine groups to Ag^I or Cu^I centers, together with the S_2 linear coordination geometry of Au^I centers, seems to be a key factor of these exclusive heterometallic reactions. However, the Ag^I-Cu^I system only gave a mixture of unidentified products. The flexibility of coordination geometries of both Ag^I and Cu^I ion probably makes the Ag^I-Cu^I heterometallic system complicated, which is distinct from the Au^I-Ag^I and Au^I-Cu^I systems.

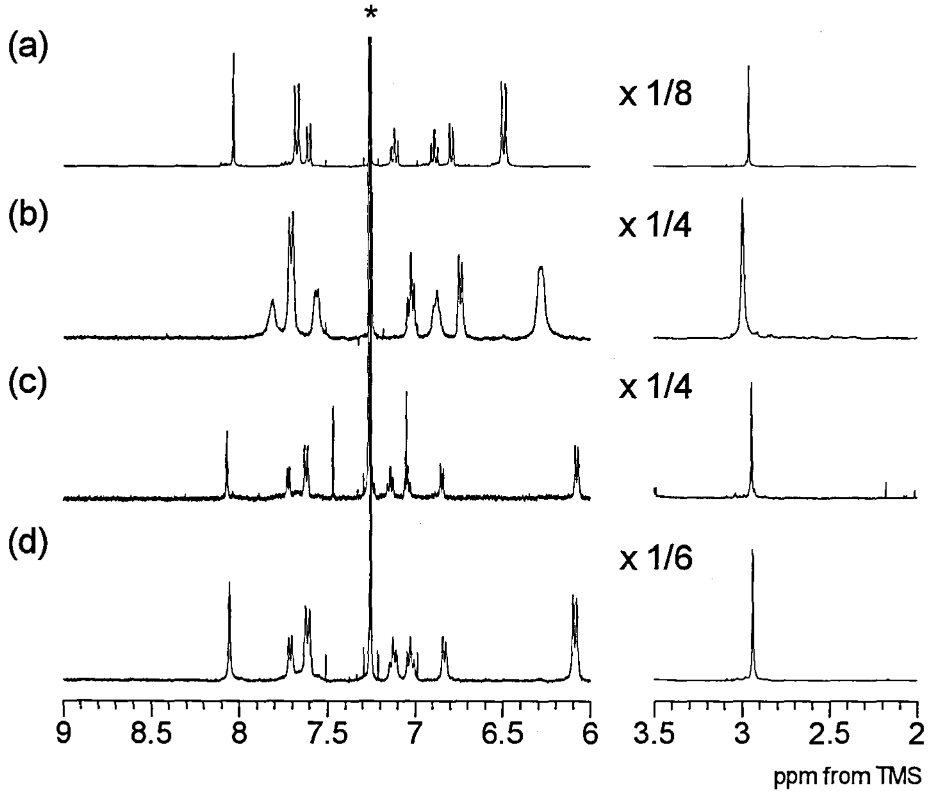
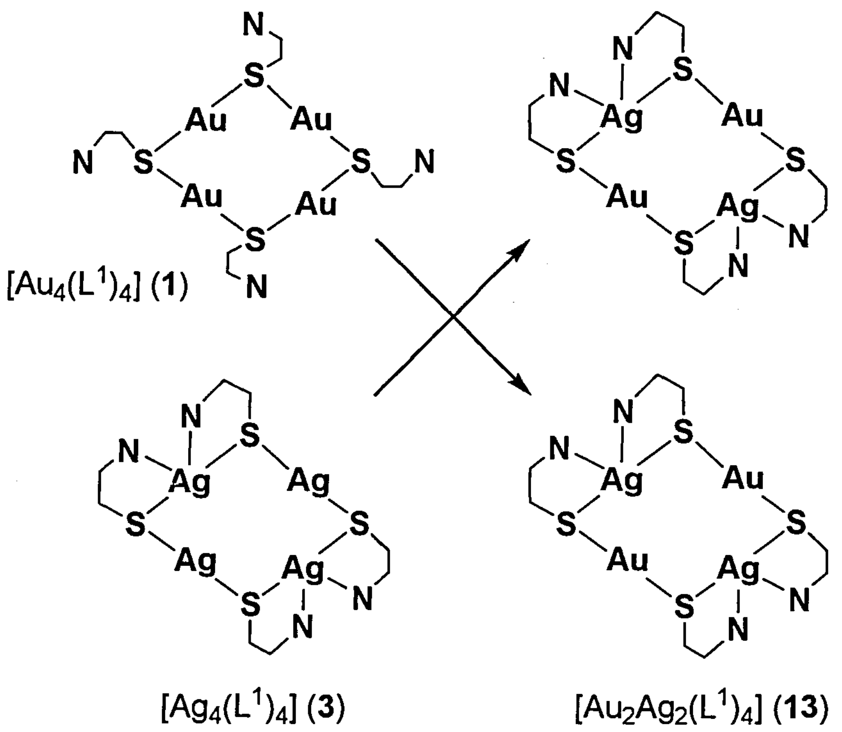


Figure 3-10. ^{1}H NMR spectra of (a) **1**, (b) **3**, (c) **13**, and (d) a 1:1 mixture of **1** and **3** in $CDCl_3$ at 30°C. (*) denotes a signal of solvent.



Scheme 3-3. A "metal-crossing" reaction between **1** and **3**.

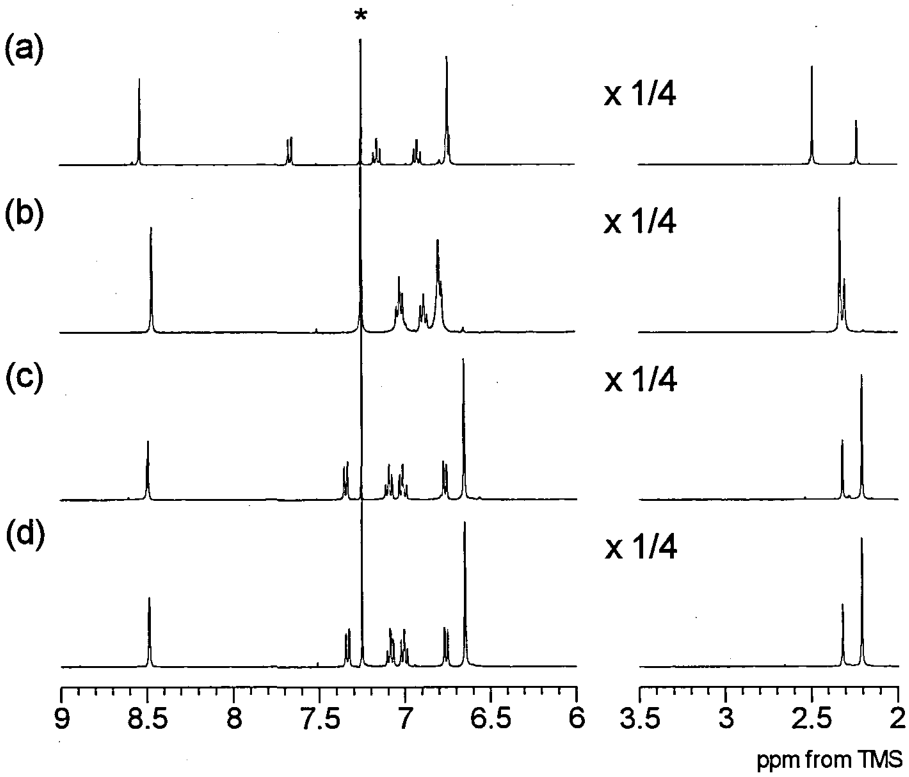


Figure 3-11. ^{1}H NMR spectra of (a) **2**, (b) **4**, (c) **14**, and (d) a 3:4 mixture of **2** and **4** in CDCl$_3$ at 30°C. (*) denotes a signal of solvent.

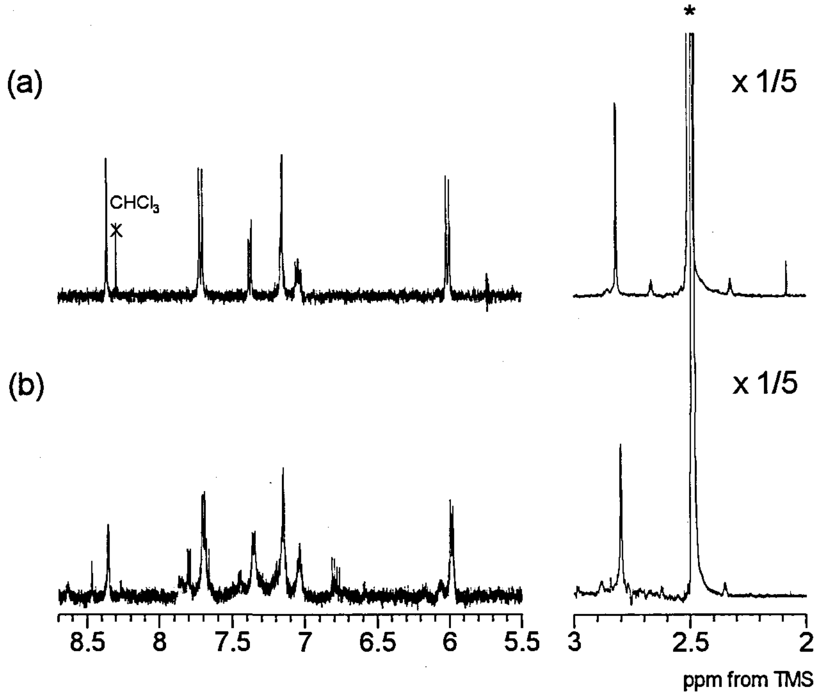


Figure 3-12. ^{1}H NMR spectra of (a) **15** and (b) a 1:1 mixture of **1** and **9** in DMSO-d_6 at 30°C. (*) denotes a signal of solvent.

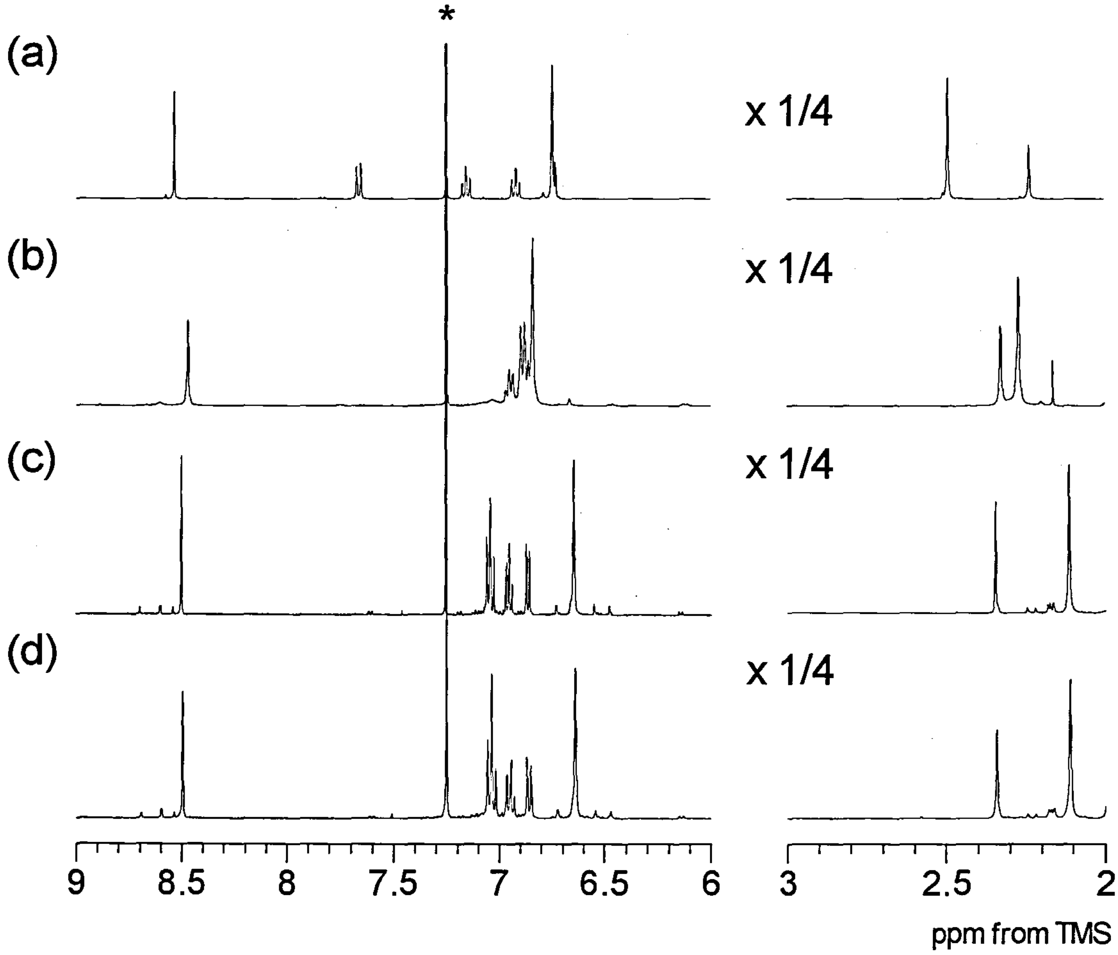


Figure 3-13. ^{1}H NMR spectra of (a) **2**, (b) **10**, (c) **16**, and (d) a 3:4 mixture of **2** and **10** in $CDCl_3$ at 30°C. (*) denotes a signal of solvent.

III-4. Summary.

In this chapter, the coordination behavior of benzothiazolines toward a mixture of two kinds of d^{10} ions of the group 11 elements was investigated. Moreover, the reactivity between homometallic complexes of Au^I, Ag^I, Cu^I ions was also investigated.

The one-pot reactions of benzothiazolines with a mixture of Au^I and Ag^I ions were led to the selectively formation of heterometallic S-bridged metallorings $[Au_2Ag_2L_4]$ ($L = L^1$ (**13**), L^2 (**14**)), showing an excellent regioselectivity. A similar regioselective formation of heterometallic S-bridged metallorings $[Au_2Cu_2L_4]$ ($L = L^1$ (**15**), L^2 (**16**)) was also observed for the reactions with a mixture of Au^I and Cu^I ions. On the other hand, the corresponding reactions with a mixture of Ag^I and Cu^I ions afforded a complicated mixture of products. It was found that one of the products is a unique 21-nuclear campanulate cluster with a campanulate-shape, $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl](ClO_4)_4$ (**17**).

Remarkably, the reactions of Au^I_4 and Ag^I_4 homometallic rings also exclusively led to the $Au^I_2Ag^I_2$ heterometallic ring structures because of the rapid recombination of core structures. As far as we know, such a metal exchange reaction between two different metallorings, which selectively forms a single kind of heterometallic ring, has never been reported. This kind of "metal-crossing" reaction was also observed in the Au^I-Cu^I system. In the Ag^I-Cu^I system, however, an analogous reaction affords a mixture of products as found in the "one-pot" reactions.

From these results, it was shown that the selective coordination of imine groups to Ag^I or Cu^I centers which can adopt three- and four-coordinate geometries, together with the S_2 linear coordination geometry of Au^I centers, is a key to the selective construction of S-bridged structures.

III-5. References.

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Table 3-1. Crystallographic data of **13**-**17**.

	13·2CH$_2$Cl$_2$	**14**	**15**·2CHCl$_3$	**16**	**17**
empirical formula	$C_{62}H_{64}Ag_2Au_2Cl_4N_8S_4$	$C_{64}H_{64}Ag_2Au_2N_4S_4$	$C_{62}H_{62}Au_2Cl_6Cu_2N_8S_4$	$C_{64}H_{64}Au_2Cu_2N_4S_4$	$C_{242}H_{243}Ag_{12}Cl_5Cu_9N_{33}O_{16}S_{16}$
fw	1800.92	1627.11	1781.15	1578.08	6426.20
size /mm^3	0.20×0.10×0.05	0.10×0.10×0.02	0.40×0.10×0.10	0.20×0.10×0.01	0.30×0.10×0.10
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	*P*-1	*P*2$_1$/*n*	*P*-1	*C*2/*c*	*C*2/*c*
a /Å	10.015(4)	11.3278(5)	8.684(3)	33.1487(6)	34.0172(10)
b /Å	12.155(5)	19.5443(13)	13.144(4)	22.6858(4)	23.8401(6)
c /Å	14.311(6)	14.1502(6)	14.618(5) Å	22.5986(4)	38.2571(9)
α /°	87.200(15)		82.937(13)		
β /°	80.614(16)	110.7050(10)	84.632(13)	110.018(8)	94.2920(10)
γ /°	68.733(17)		74.993(13)		
V /Å^3	1601.5(11)	2930.4(3)	1596.0(9)	15967.5(5)	30938.5(14)
Z	1	2	1	8	4
T /K	200(2)	200(2)	200(2)	200(2)	200(2)
R(int)	0.0713	0.1336	0.0689	0.0345	0.1051
$\rho_{\text{calcd.}}$ /g cm^{-3}	1.867	1.844	1.853	1.313	1.380
μ (Mo Ka), mm^{-1}	5.512	5.835	5.668	4.328	1.548
θ_{Max}	55.0	54.9	54.9	55.0	55.0
R_1 (I>2σ(I))[a]	0.044	0.063	0.040	0.048	0.092
Rw[b]	0.126	0.130	0.101	0.147	0.325

[a] $R_1 = \Sigma|(|F_o|-|F_c|)| / \Sigma(|F_o|)$. [b] $Rw = [\Sigma w(F_o^2-F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table 3-2. Selected bond distances and angles of **13**·$2CH_2Cl_2$.

	Bond distances (Å)		
Au(1)-S(1)	2.2911(19)	Ag(1)-N(3)	2.544(6)
Au(1)-S(2)	2.3074(19)	Ag(1)-N(1)#1	2.677(5)
Ag(1)-S(1)#1	2.429(2)	Au(1)-Ag(1)	3.0536(12)
Ag(1)-S(2)	2.494(2)		
	Angles (°)		
S(1)-Au(1)-S(2)	175.86(6)	Au(1)-S(2)-Ag(1)	78.88(6)
S(1)#1-Ag(1)-S(2)	137.42(6)	Au(1)-S(1)-Ag(1)#1	103.79(7)

#1 -x,-y+2,-z+1

Table 3-3. Selected bond distances and angles of **14**.

	Bond distances (Å)		
Au(1)-S(1)	2.290(2)	Ag(1)-N(2)	2.377(7)
Au(1)-S(2)#1	2.294(2)	Au(1)-Ag(1)	3.1970(8)
Ag(1)-S(1)	2.398(2)	Au(1)-Ag(1)#1	3.0602(7)
Ag(1)-S(2)	2.555(2)		
	Angles (°)		
S(1)-Au(1)-S(2)#1	179.46(9)	Au(1)-S(1)-Ag(1)	85.94(7)
S(1)-Ag(1)-S(2)	137.18(9)	Ag(1) -S(2)-Ag(1)#1	78.07(7)

#1 -x,-y+1,-z

Table 3-4. Selected bond distances and angles of **15**·$2CHCl_3$.

	Bond distances (Å)		
Au(1)-S(1)	2.2818(15)	Cu(1)-N(1)	2.195(4)
Au(1)-S(2)#1	2.3075(15)	Cu(1)-N(3)	2.121(4)
Cu(1)-S(1)	2.2892(18)	Au(1)-Cu(1)#1	3.1163(11)
Cu(1)-S(2)	2.3379(16)		
	Angles (°)		
S(1)-Au(1)-S(2)#1	176.44(4)	Au(1)-S(1)-Cu(1)	117.99(6)
S(1)-Cu(1)-S(2)	111.10(5)	Au(1)#1-S(2)-Cu(1)	84.26(5)

#1 -x+1,-y+1,-z+1

Table 3-5. Selected bond distances and angles of **16**.

	Bond distances (Å)		
Au(1)-S(1)	2.2955(16)	Cu(1)-N(3)	2.148(5)
Au(1)-S(2)	2.2972(16)	Cu(2)-N(4)	2.137(6)
Au(2)-S(4)	2.2930(18)	Cu(2)-N(2)	2.155(6)
Au(2)-S(3)	2.2946(18)	Au(1)-Au(2)	3.1810(4)
Cu(1)-S(1)	2.297(2)	Au(1)-Cu(2)	2.8444(8)
Cu(1)-S(3)	2.3199(19)	Au(1)-Cu(1)	2.9782(9)
Cu(2)-S(4)	2.2981(19)	Au(2)-Cu(1)	2.8865(8)
Cu(2)-S(2)	2.3145(19)	Au(2)-Cu(2)	2.9931(8)
Cu(1)-N(1)	2.141(6)		
	Angles (°)		
S(1)-Au(1)-S(2)	177.96(6)	Au(1)-S(1)-Cu(1)	80.86(6)
S(4)-Au(2)-S(3)	177.71(7)	Au(1)-S(2)-Cu(2)	76.16(5)
S(1)-Cu(1)-S(3)	142.08(7)	Au(2)-S(3)-Cu(1)	77.44(6)
S(4)-Cu(2)-S(2)	141.90(7)	Au(2)-S(4)-Cu(2)	81.38(6)

#1 -x+1,y,-z+1/2

Table 3-6. Selected bond distances and angles of **17**.

Bond distances (Å)

Ag(1)-S(1)	2.470(3)	Ag(6)-S(8)	2.559(2)
Ag(1)-S(2)	2.470(2)	Ag(6)-Ag(3)#1	3.0280(10)
Ag(1)-S(4)	2.771(2)	Ag(6)-Cu(3)	3.0450(12)
Ag(1)-N(1)	2.349(8)	Cu(1)-S(1)	2.313(3)
Ag(1)-Ag(2)#1	3.1218(11)	Cu(1)-S(1)#1	2.313(3)
Ag(1)-Cu(1)	3.0824(10)	Cu(1)-N(17)	2.27(2)
Ag(2)-S(1)	2.669(3)	Cu(1)-Ag(1)#1	3.0824(10)
Ag(2)-S(2)#1	2.519(2)	Cu(1)-Ag(2)#1	2.9556(13)
Ag(2)-S(5)	2.612(2)	Cu(2)-S(2)	2.279(3)
Ag(2)-Cl(1)	2.8534(19)	Cu(2)-S(3)	2.307(3)
Ag(2)-Ag(1)#1	3.1218(11)	Cu(2)-N(3)	2.131(8)
Ag(2)-Ag(3)#1	3.2387(11)	Cu(2)-N(5)	2.071(9)
Ag(2)-Cu(1)	2.9556(13)	Cu(3)-S(5)	2.559(2)
Ag(3)-S(3)	2.440(2)	Cu(3)-S(7)	2.260(2)
Ag(3)-S(4)	2.411(2)	Cu(3)-S(8)	2.472(2)
Ag(3)-Cu(2)	2.8381(13)	Cu(3)-N(9)	2.006(7)
Ag(3)-Ag(2)#1	3.2387(11)	Cu(3)-N(5)	10.152(8)
Ag(3)-Ag(6)#1	3.0280(10)	Cu(4)-S(6)#1	2.248(2)
Ag(4)-S(4)	2.687(2)	Cu(4)-S(6)	2.781(2)
Ag(4)-S(5)	2.472(2)	Cu(4)-S(7)	2.308(2)
Ag(4)-N(7)	2.284(7)	Cu(4)-N(11)	2.004(8)
Ag(4)-Cu(3)	3.0965(13)	Cu(4)-Cu(4)#1	2.772(2)
Ag(5)-S(4)	2.595(2)	Cu(5)-S(8)	2.251(2)
Ag(5)-S(6)	2.589(2)	Cu(5)-N(13)	1.950(8)
Ag(5)-S(7)	2.563(2)	Cu(5)-N(15)	2.071(7)
Ag(5)-Cl(1)	2.734(2)	Cu(5)-Cu(3)	2.7453(15)
Ag(5)-Ag(3)	3.1208(10)	Cl(1)-Ag(5)#1	2.734(2)
Ag(5)-Ag(4)	2.9518(10)	Cl(1)-Ag(2)#1	2.8534(19)
Ag(5)-Cu(4)	2.9049(14)	S(6)-Cu(4)#1	2.248(2)
Ag(6)-S(3)#1	2.598(2)	S(6)-Ag(6)#1	2.546(2)
Ag(6)-S(5)	2.735(2)	S(2)-Ag(2)#1	2.519(2)
Ag(6)-S(6)#1	2.546(2)	S(3)-Ag(6)#1	2.598(2)

Angles (°)

S(7)-Ag(5)-S(6)	103.74(7)	S(5)-Ag(4)-S(4)	136.90(7)
S(7)-Ag(5)-S(4)	120.57(7)	S(4)-Ag(3)-S(3)	164.36(8)
S(6)-Ag(5)-S(4)	123.23(7)	S(4)-Ag(3)-Cu(2)	114.00(6)
S(7)-Ag(5)-Cl(1)	125.01(5)	S(3)-Ag(3)-Cu(2)	51.17(6)
S(6)-Ag(5)-Cl(1)	96.75(6)	S(2)#1-Ag(2)-S(5)	123.69(8)
S(4)-Ag(5)-Cl(1)	85.96(7)	S(2)#1-Ag(2)-S(1)	130.49(9)
N(7)-Ag(4)-S(5)	149.70(18)	S(5)-Ag(2)-S(1)	90.68(8)
N(7)-Ag(4)-S(4)	73.39(18)	S(2)#1-Ag(2)-Cl(1)	129.37(6)

S(5)-Ag(2)-Cl(1)	81.74(6)	N(3)-Cu(2)-S(2)	85.6(3)
S(1)-Ag(2)-Cl(1)	85.76(7)	N(5)-Cu(2)-S(3)	87.3(3)
S(6)#1-Ag(6)-S(8)	116.79(7)	N(3)-Cu(2)-S(3)	121.5(2)
S(6)#1-Ag(6)-S(3)#1	121.07(7)	S(2)-Cu(2)-S(3)	121.13(9)
S(8)-Ag(6)-S(3)#1	112.97(7)	Ag(4)-S(5)-Cu(3)	75.96(6)
S(6)#1-Ag(6)-S(5)	112.11(7)	Ag(4)-S(5)-Ag(2)	95.91(7)
S(8)-Ag(6)-S(5)	97.73(7)	Cu(3)-S(5)-Ag(2)	165.77(9)
S(3)#1-Ag(6)-S(5)	89.77(8)	Ag(4)-S(5)-Ag(6)	129.60(8)
N(1)-Ag(1)-S(1)	77.6(2)	Cu(3)-S(5)-Ag(6)	70.14(6)
N(1)-Ag(1)-S(2)	132.9(2)	Ag(2)-S(5)-Ag(6)	108.19(7)
S(1)-Ag(1)-S(2)	144.24(9)	Cu(3)-S(7)-Cu(4)	124.26(9)
N(1)-Ag(1)-S(4)	114.9(2)	Cu(3)-S(7)-Ag(5)	111.01(9)
S(1)-Ag(1)-S(4)	96.78(8)	Cu(4)-S(7)-Ag(5)	73.00(6)
N(17)-Cu(1)-S(1)#1	104.36(8)	Ag(3)-S(4)-Ag(5)	77.03(6)
N(17)-Cu(1)-S(1)	104.36(8)	Ag(3)-S(4)-Ag(4)	141.59(9)
S(1)#1-Cu(1)-S(1)	151.28(15)	Ag(5)-S(4)-Ag(4)	67.92(5)
N(13)-Cu(5)-N(15)	140.2(3)	Ag(3)-S(4)-Ag(1)	101.19(8)
N(13)-Cu(5)-S(8)	130.7(2)	Ag(5)-S(4)-Ag(1)	128.57(9)
N(15)-Cu(5)-S(8)	88.3(2)	Ag(4)-S(4)-Ag(1)	89.16(7)
N(9)-Cu(3)-S(7)	145.0(2)	Cu(4)#1-S(6)-Ag(6)#1	100.25(8)
N(9)-Cu(3)-S(8)	109.6(2)	Cu(4)#1-S(6)-Ag(5)	113.58(9)
S(7)-Cu(3)-S(8)	101.42(8)	Ag(6)#1-S(6)-Ag(5)	111.07(9)
N(9)-Cu(3)-S(5)	82.97(19)	Cu(4)#1-S(6)-Cu(4)	65.91(7)
S(7)-Cu(3)-S(5)	104.55(8)	Ag(6)#1-S(6)-Cu(4)	159.87(9)
S(8)-Cu(3)-S(5)	104.91(8)	Ag(5)-S(6)-Cu(4)	65.38(6)
N(9)-Cu(3)-N(5)	106.9(2)	Cu(5)-S(8)-Cu(3)	70.90(7)
S(7)-Cu(3)-N(5)	45.91(8)	Cu(5)-S(8)-Ag(6)	132.67(10)
S(8)-Cu(3)-N(5)	143.18(8)	Cu(3)-S(8)-Ag(6)	74.48(7)
S(5)-Cu(3)-N(5)	74.99(8)	Cu(2)-S(2)-Ag(1)	143.30(12)
N(11)-Cu(4)-S(6)#1	138.7(2)	Cu(2)-S(2)-Ag(2)#1	106.49(9)
N(11)-Cu(4)-S(7)	104.6(2)	Ag(1)-S(2)-Ag(2)#1	77.46(7)
S(6)#1-Cu(4)-S(7)	114.26(9)	Cu(2)-S(3)-Ag(3)	73.37(7)
N(11)-Cu(4)-S(6)	80.1(2)	Cu(2)-S(3)-Ag(6)#1	136.75(11)
S(6)#1-Cu(4)-S(6)	101.81(8)	Ag(3)-S(3)-Ag(6)#1	73.81(6)
S(7)-Cu(4)-S(6)	105.20(8)	Cu(1)-S(1)-Ag(1)	80.17(10)
N(5)-Cu(2)-N(3)	111.8(3)	Cu(1)-S(1)-Ag(2)	72.38(8)
N(5)-Cu(2)-S(2)	133.3(3)	Ag(1)-S(1)-Ag(2)	129.66(12)

#1 -x,y,-z+1/2

Chapter IV. Concluding Remarks.

In this study, the reactions of benzothiazolines with $\mathrm{Au^I}$, $\mathrm{Ag^I}$, and $\mathrm{Cu^I}$ ions were investigated, in order to clarify the coordination behavior of the iminothiophenolate ligands to the d^{10} metal ions of group 11 elements. A total of 19 d^{10} metal complexes, including five heterodimetallic ones, were newly synthesized and were structurally characterized by X-ray crystallography and spectroscopies. As a result, it was found that the structures of the resulting multinuclear complexes are strongly dependent not only on the employed metal ions, but also on the substituent groups of benzothiazolines and the presence/absence of halide ions.

In Chapter II, coordination behaviors of iminothiophenolate ligands derived from benzothiazolines toward each of $\mathrm{Au^I}$, $\mathrm{Ag^I}$, and $\mathrm{Cu^I}$ ions were investigated, and S-bridged multinuclear complexes consisting of metalloring cores $\{\mathrm{M^I}_n\mathrm{S}_n\}$ were constructed. The reactions of benzothiazolines with $\mathrm{Au^I}$ ions afforded the S-bridged tetranuclear cyclic complexes, $[\mathrm{Au_4L_4}]$ ($\mathrm{L} = \mathrm{L^1}$ (**1**), $\mathrm{L^2}$ (**2**)), having an $\{\mathrm{Au^I}_4\mathrm{S}_4\}$ metalloring that is very close to a regular square. In the complexes, each ligand bound to $\mathrm{Au^I}$ ions only through its thiolate group to adopt a μ_2-κ^1S:κ^1S coordination mode, and its imine group uses not participated in the coordination. No significant substituent effect was observed in this $\mathrm{Au^I}$ system. The reactions of benzothiazolines with $\mathrm{Ag^I}$ ions gave similar S-bridged tetranuclear cyclic complexes, $[\mathrm{Ag_4L_4}]$ ($\mathrm{L} = \mathrm{L^1}$ (**3**), $\mathrm{L^2}$ (**4**), $\mathrm{L^3}$ (**5**), $\mathrm{L^4}$ (**6**), $\mathrm{L^5}$ (**7**)) with an $\{\mathrm{Ag^I}_4\mathrm{S}_4\}$ metalloring. In the complexes, however, each imine group coordinated to an $\mathrm{Ag^I}$ center in a μ_2-κ^1S:κ^2N,S coordination mode, which is in sharp contrast to the $\mathrm{Au^I}$ complexes. For the $\mathrm{Ag^I}$ complexes, there exist two types of $\{\mathrm{Ag^I}_4\mathrm{S}_4\}$ metallorings that are discriminated by a coordination environment around $\mathrm{Ag^I}$ ions. One is 2,4-coordination manner observed for **3**, **5**, and **6**, and the other is 3,3-coordination manner observed for **4** and **7**. This result is indicative of the flexible coordination behavior of $\mathrm{Ag^I}$ ions, as well as the existence of some substituent effect in the $\mathrm{Ag^I}$ system. The reactions of benzothiazolines with $\mathrm{Cu^I}$ ions formed not only simple metalloring structures but also cluster structures with a high nuclearity. It was found that their structures are strongly dependent on the bulkiness of substituent groups on the iminothiophenolate ligands. When 2-(4-dimethylaminophenyl)benzothiazoline having a relatively small substituent group was treated with Cu^I ions, two kind of S-bridged clusters, $[Cu_{10}(L^1)_9]PF_6$ **(8)** and $[Cu_8(L^1)_8](PF_6)_2$ **(9)**, were formed by changing the solvent. On the other hand, the use of benzothiazolines with a relatively large substituent group, 2-(2,4,6-trimethylphenyl)benzothiazoline or 2-(9-anthracenyl)-benzothiazoline, prevented the formation of cluster structures due to the steric constraint, forming simple metalloring structures in $[Cu_3(L^2)_3]$ **(10)** and $[Cu_4(L^4)_4]$ **(11)**. In these Cu^I complexes, each ligand adopt $\mu_2\text{-}\kappa^1S{:}\kappa^2N,S$ or $\mu_3\text{-}\kappa^1S{:}\kappa^1S{:}\kappa^2N,S$ coordination mode with the imine groups coordinating to Cu^I ions. It was found that the reactions of 2-(4-dimethylaminophenyl)benzothiazoline with Cu^I ion in the presence of halide ions give hexadecanuclear spherical clusters, $[Cu_{16}(L^1)_{12}X](PF_6)_3$ (X = Cl **(12-Cl)**, Br **(12-Br)**, and I **(12-I)**), in which four $\{Cu^I_3S_3\}$ metallorings are assembled around a central halide ion. To the best of our knowledge, this is the first example of the formation of a copper-thiolato system with a high nuclearity, which is controlled by the presence/absence of halide ions. These results clearly indicate that Cu^I systems with iminothiophenolates are controlled not only by solvent and substituent effect but also by the template effect of halide ions.

In Chapter III, the reactions of benzothiazolines with a mixture of two of three d^{10} metal ions of group 11 elements were examined using “one-pot” and “metal-crossing” methods. In the Au^I-Ag^I and Au^I-Cu^I systems, it was found that the “one-pot” reactions afford four S-bridged tetranuclear metallorings, $[Au_2Ag_2L_4]$ (L = L^1 **(13)** and L^2 **(14)**) and $[Au_2Cu_2L_4]$ (L = L^1 **(15)** and L^2 **(16)**). In these tetranuclear metallorings, two kinds of metal ions were arranged in an alternate fashion (AuMAuM-type, M = Ag or Cu), and the imine groups selectively coordinated to Ag^I or Cu^I ions. Moreover, the mixing of homometallic rings with different metal ions in solution led to the selective formation of the heterometallic rings, indicative of the recombination of two homometallic rings with the regioselective metal arrangement. To our knowledge, such a regioselective metal-exchange between two metallorings with different metal ions has never been reported. On the other hand, such a selective formation of the corresponding heterometallic rings was not observed in the Ag^I-Cu^I system either by “one-pot” or by “metal-crossing” reaction, and a complicated mixture containing the 21-nuclear campanulate-shape cluster, $[Ag_{12}Cu_9(L^1)_{16}(CH_3CN)Cl](ClO_4)_4$ **(17)**, was formed. From these observations, it is seen that the selective coordination of imine groups to Ag^I or Cu^I centers, together with the S_2 linear coordination geometry of Au^I centers, is a key factor to the selective formation of the heterometallic compounds with the thermodynamically stable $\{Au^I_2M^I_2S_4\}$ ring.

Finally, the present work, which elucidates the reactivity of iminothiophenolate ligand derived from benzothiazolines toward the d^{10} ions of the group 11 transition metals, should contribute not only to the development of the fundamental coordination chemistry of iminothiophenolates but also to the new synthetic strategy of heterometallic rings through an unprecedented "metal-crossing" reaction.

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