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# Thiolato-bridged $Au^I{}_2Cu^I{}_2$ and $Cu^I{}_4$ Metallorings Derived from Benzothiazoline: Can Gold(I) Plus Copper(I) Make Silver(I)?

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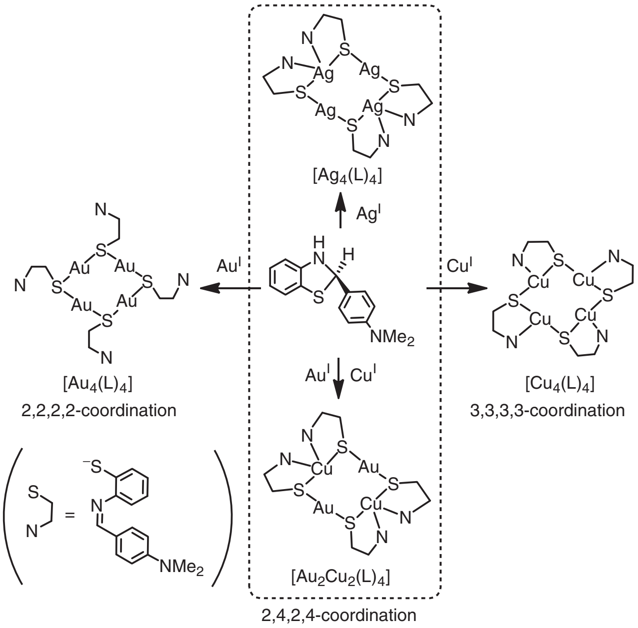
A thiolato-bridged $Au^I{}_2Cu^I{}_2$ metalloring compound, $[Au_2Cu_2(L)_4]$ ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$), together with an analogous $Cu^I{}_4$ compound, $[Cu_4(L)_4]$, was newly prepared from 2-(4-dimethylaminophenyl)benzothiazoline. The $Au^I{}_2Cu^I{}_2$ compound was found to show structural and spectroscopic features comparable well with those of $[Ag_4(L)_4]$, rather than those of $[Au_4(L)_4]$ and $[Cu_4(L)_4]$.

There has been considerable research interest in multinuclear coordination compounds of group 11 elements in recent years.[1] In particular, heterometallic compounds containing two or three kinds of group 11 metal ions are of much interest due to their fascinating structural features and unique chemical and physicochemical properties.[2] In general, this class of compounds can be synthesized by one-pot reactions of selected organic ligands with a mixture of group 11 metal ions or by stepwise reactions via homometallic precursors with a different group 11 metal ion. However, the former reactions commonly require troublesome separation processes because of the formation of a mixture of several homometallic and heterometallic species, while the latter reactions require well-designed, controlled reaction pathways. Thus, the finding of a coordination system that exclusively affords a single heterometallic species from a mixture of different kinds of group 11 metal ions remains a great challenge.

In our successive study on the reactivity of 2-substituted benzothiazolines toward transition-metal ions,[3] we have recently synthesized thiolato-bridged tetranuclear complexes, $[Au_4(L)_4]$ and $[Ag_4(L)_4]$ ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$), by the simple reactions of 2-(4-dimethylaminophenyl)benzothiazoline with gold(I) or silver(I) in chloroform in a 1:1 ratio.[4] In addition, we have found that an analogous tetranuclear complex containing both $Au^I$ and $Ag^I$ ions, $[Au_2Ag_2(L)_4]$, is selectively produced by a similar reaction with a 1:1 mixture of gold(I) and silver(I).[4] This result prompted us to investigate whether this synthetic method is applicable to the preparation of a heterometallic complex containing both of $Au^I$ and $Cu^I$. In this paper, we report that the use of a 1:1 mixture of gold(I) and copper(I), instead of a mixture of gold(I) and silver(I), indeed results in the production of an expected heterometallic complex, $[Au_2Cu_2(L)_4]$. The preparation of an analogous $Cu^I{}_4$ complex, $[Cu_4(L)_4]$, from 2-(4-dimethylaminophenyl)benzothiazoline is also reported. Notably, $[Au_2Cu_2(L)_4]$ was found to exhibit structural and spectroscopic features that are comparable well with those of $[Ag_4(L)_4]$, rather than those of $[Au_4(L)_4]$ and $[Cu_4(L)_4]$ (Scheme 1). As far as we know, this is the first report that points out the possible creation of characteristics of a silver(I) compound by the introduction of a mixture of $Au^I$ and $Cu^I$ ions, in place of $Ag^I$ ions.



**Scheme 1.** The $Au^I{}_4$, $Ag^I{}_4$, $Cu^I{}_4$, and $Au^I{}_2Cu^I{}_2$ metalloring structures with iminothiolates.

Treatment of a chloroform solution of 2-(4-dimethylaminophenyl)benzothiazoline, a chloroform solution of chloro(tetrahydrothiophene)gold(I), and an acetonitrile solution of tetraacetonitrilecopper(I) perchlorate in a 2:1:1 ratio in the presence of $NEt_3$ gave a dark orange solution, from which orange crystals ($\mathbf{1}\cdot 2CHCl_3$) suitable for X-ray crystallography were isolated by slow evaporation at room temperature.[5] X-ray fluorescence analysis of this compound revealed the presence of Au and Cu, and its elemental analysis was consistent with a formula containing iminothiolate ligands ($L = (C_6H_4NMe_2)CH{=}N(C_6H_4)S^-$) and $Au^I$ and $Cu^I$ atoms in a 2:1:1 ratio.[6] Single-crystal X-ray analysis revealed that **1** contains two $Au^I$ and two $Cu^I$ atoms in combination with four L ligands, with the lack of any counter ions.[7] As shown in Figure 1, the $Au^I$ and $Cu^I$ atoms are alternately linked by four S atoms from four L ligands, forming a thiolato-bridged $Au^I{}_2Cu^I{}_2$ metalloring structure with a $C_i$ symmetry. Each L ligand adopts a $\mu_2$-$\kappa^1S{:}\kappa^2N,S$ coordination mode, in which its imine group coordinates to a $Cu^I$ atom (av $Cu–N = 2.16(5)$ Å) and its thiolato group bridges $Au^I$ and $Cu^I$ atoms (av $Au–S = 2.295(18)$ Å, $Cu–S = 2.31(3)$ Å). As a result, two $Cu^I$ atoms are situated in an $N_2S_2$ tetrahedral geometry ($N–Cu–N = 117.88(14)°$, $S–Cu–S = 111.10(5)°$), while two $Au^I$ atoms are in an $S_2$ linear geometry ($S–Au–S = 176.44(4)°$). The preference of linear and tetrahedral geometries for $Au^I$ and $Cu^I$, as well as the high affinity of an imine group to a $Cu^I$ center

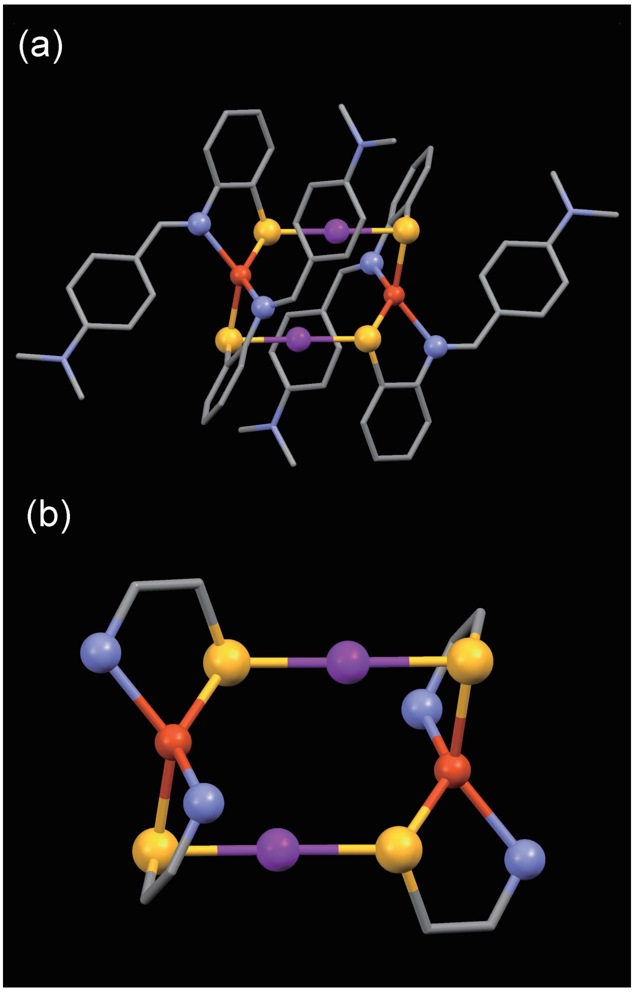


**Figure 1.** Perspective views of (a) **1** and (b) its core structure; $\mathrm{Au^I}$: purple, $\mathrm{Cu^I}$: brown, N: blue, S: yellow, C: gray. H atoms are omitted for clarity.

rather than to an $\mathrm{Au^I}$ center, accounts for the formation of this metalloring structure. Despite the $C_i$ symmetric structure in crystal **1**, the $^1$H NMR spectrum of **1** in $CDCl_3$ gave only a single set of signals for four L ligands (Figure S1a),[5] suggestive of the flexible nature of its $\mathrm{Au^I_2Cu^I_2S_4}$ metalloring framework with an averaged $C_{2h}$ symmetry in solution.

It is possible that three heterometallic species, $[\mathrm{Au_3Cu_1(L)_4}]$, $[\mathrm{Au_2Cu_2(L)_4}]$, and $[\mathrm{Au_1Cu_3(L)_4}]$, besides two homometallic species, $[\mathrm{Au_4(L)_4}]$ and $[\mathrm{Cu_4(L)_4}]$, are formed from L ligands in combination with a 1:1 mixture of $\mathrm{Au^I}$ and $\mathrm{Cu^I}$ ions. In addition, two isomeric forms that are discriminated by the arrangement of $\mathrm{Au^I}$ and $\mathrm{Cu^I}$ ions, AuAuCuCu-type and AuCuAuCu-type, are possible for $[\mathrm{Au_2Cu_2(L)_4}]$. However, the present reaction exclusively produced $[\mathrm{Au_2Cu_2(L)_4}]$ with an AuCuAuCu-type arrangement in a moderate yield of ca. 50%. Since the $^1$H NMR spectrum of a reaction mixture of 2-(4-dimethylaminophenyl)-benzothiazoline, triethylamine, chloro(tetrahydrothiophene)-gold(I), and tetraacetonitrilecopper(I) perchlorate in a 2:2:1:1 ratio in $CDCl_3/CD_3CN$ is indicative of the formation of a complex mixture with no obvious preference for a single species (Figure S1b),[5] the selective isolation of **1** is attributed to its less solubility in solution. This is different from the corresponding reaction with a mixture of gold(I) and silver(I), in which a single species of $[\mathrm{Au_2Ag_2(L)_4}]$ with an AuAgAuAg-type arrangement is selectively formed in solution.[4,8] The affinity of an imine group to a $\mathrm{Cu^I}$ center, which is much higher than to an $\mathrm{Ag^I}$ center, seems to prevent the conversion of some kinetic products to the thermodynamically stable product of **1** in solution.

To obtain a homometallic $\mathrm{Cu^I_4}$ metalloring compound, a chloroform solution of 2-(4-dimethylaminophenyl)benzothiazoline was treated with an acetonitrile solution of tetraacetonitrilecopper(I) perchlorate in a 1:1 ratio. However, this reaction did not give $[\mathrm{Cu_4(L)_4}]$ but produced a brown compound of $[\mathrm{Cu_8(L)_8}](\mathrm{ClO_4})$ that has been obtained by the 2:1 reaction of 2-(4-dimethylaminophenyl)benzothiazoline with copper(II) acetate in 1,2-dichloroethane.[3c] After several trials, an orange compound **2**, which is assignable to have a neutral formula of $[\mathrm{Cu^I(L)}]_n$ based on the elemental analysis and IR spectrum that is essentially the same as that of **1** (Figure S2),[5] was obtained by the reaction of 2-(4-dimethylaminophenyl)benzothiazoline with copper(II) acetate in a 2:1 ratio in toluene.[5,9] Although the characterization of **2** by means of the NMR spectroscopy was precluded owing to its poor solubility in common solvents and its instability in solution,[10] an expected $\mathrm{Cu^I_4}$ metalloring structure was established by single-crystal X-ray analysis.[11] In **2**, four Cu atoms are bridged by four S atoms from four L ligands to form a tetranuclear metalloring structure with an $S_4$ symmetry (Figure 2). Each Cu atom in **2** is in a +1 oxidation state, as evidenced by the lack of any counter cations. Thus, it is seen that 2-(4-dimethylaminophenyl)benzothiazoline acts not only as a ligand precursor but also as a reducing agent for copper(II).[3c] The successful isolation of **2** by the use of toluene as a reaction medium, instead of 1,2-dichloroethane, is most likely due to the insolubility of **2** in this solvent, which leads to the precipitation of **2** prior to its conversion into $[\mathrm{Cu_8(L)_8}]^+$ in solution. Each L ligand in **2** also adopts a $\mu_2$-$\kappa^1S{:}\kappa^2N,S$ coordination mode (av Cu–S = 2.211(4) Å, av Cu–N = 2.140(9) Å), like in **1**. However, in **2**, four imine groups from four L ligands bind to four different $\mathrm{Cu^I}$ atoms, and each $\mathrm{Cu^I}$ atom is situated in an $NS_2$ trigonal-planar geometry (S–Cu–S = 146.59(8)°, N–Cu–S = 117.9(3) and 87.8(3)°). Thus, the four bridging S atoms in **2** are situated in a square arrangement, which is distinct from an arrangement of parallelogram found in **1**.

Previously, we have shown that the homometallic $\mathrm{Au^I_4}$ and $\mathrm{Ag^I_4}$ compounds, $[\mathrm{Au_4(L)_4}]$ and $[\mathrm{Ag_4(L)_4}]$, also have a metalloring structure, in which four metal atoms are bridged by four S atoms from four L ligands, as in the case of $[\mathrm{Cu_4(L)_4}]$ (**2**).[4] However, in $[\mathrm{Au_4(L)_4}]$, all four $\mathrm{Au^I}$ atoms adopt a two-coordination geometry, whereas two of four $\mathrm{Ag^I}$ atoms adopt a two-coordination geometry and the other $\mathrm{Ag^I}$ atoms have a four-coordination geometry in $[\mathrm{Ag_4(L)_4}]$ (Figure S3).[5] The 2,2,2,2-coordination in $[\mathrm{Au_4(L)_4}]$ and the 2,4,2,4-coordination in $[\mathrm{Ag_4(L)_4}]$ are both different from the 3,3,3,3-coordination found in **2**, in which four $\mathrm{Cu^I}$ atoms are unified to have a three-coordination geometry. It should be noted that the 2,4,2,4-coordination pattern in $[\mathrm{Ag_4(L)_4}]$ is the same as that in $[\mathrm{Au_2Cu_2(L)_4}]$ (**1**). In addition, the four bridging S atoms in $[\mathrm{Ag_4(L)_4}]$ are in an arrangement of parallelogram like in **1**, whereas those in $[\mathrm{Au_4(L)_4}]$ are in a square arrangement like in **2**. Thus, the overall metalloring structure in $[\mathrm{Ag_4(L)_4}]$ is well comparable with that in $[\mathrm{Au_2Cu_2(L)_4}]$ (**1**), rather than those in

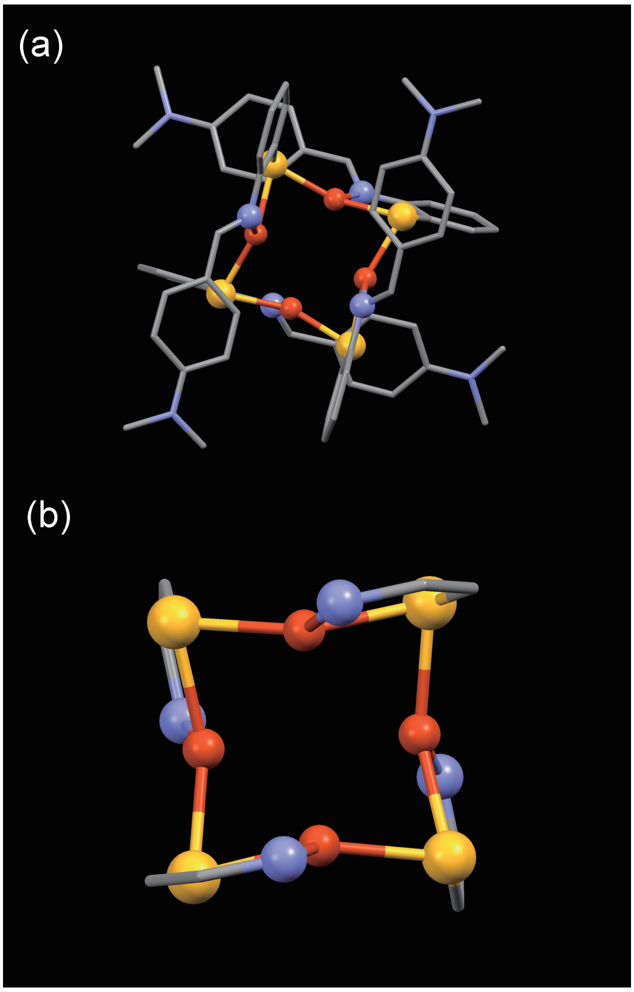


**Figure 2.** Perspective views of (a) **2** and (b) its core structure; $Cu^{I}$: brown, N: blue, S: yellow, C: gray. H atoms are omitted for clarity.

$[Au_4(L)_4]$ and $[Cu_4(L)_4]$ (**2**). Besides the structural feature, the similarity between $[Ag_4(L)_4]$ and $[Au_2Cu_2(L)_4]$ (**1**) was noticed in the solid-state electronic spectra. That is, the diffuse reflection spectrum of **1** is dominated by an intense band at 392 nm,[12] the peak position of which is very close to that for $[Ag_4(L)_4]$ (390 nm), rather than those for $[Au_4(L)_4]$ (380 nm) and **2** (402 nm) (Figure S4).[5]

In summary, we showed that a single species of $[Au_2Cu_2(L)_4]$, in which $Au^{I}$ and $Cu^{I}$ atoms are alternately bridged by S atoms in a cyclic form, is selectively isolated from the reaction of 2-(4-dimethylaminophenyl)benzothiazoline with a mixture of gold(I) and copper(I). An analogous homometallic $Cu^{I}_4$ metalloring compound, $[Cu_4(L)_4]$, was also obtained by the reaction with copper(II) when toluene was used as a reaction solvent. What is the most remarkable finding is that the structural feature of $[Au_2Cu_2(L)_4]$, as well as its electronic spectral feature, is similar to that of $[Ag_4(L)_4]$, rather than those of $[Au_4(L)_4]$ and $[Cu_4(L)_4]$. This finding indicates for the first time that a coordination compound bearing characteristics of a homometallic silver(I) species is possibly created from gold(I) and copper(I), providing a significant insight into the development of modern "alchemy" that meets the demand of alternatives for rare metals or harmful elements.[13]

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

6 Anal. Calcd for $\mathbf{1}\cdot 2CHCl_3$: C, 41.81; H, 3.51; N, 6.29%. Found: C, 41.75; H, 3.51; N, 6.41%.

7 Crystal data for $\mathbf{1}\cdot 2CHCl_3$, Triclinic, $P\bar{1}$, $a = 8.684(3)$ Å, $b = 13.144(4)$ Å, $c = 14.618(5)$ Å, $\alpha = 82.937(13)°$, $\beta = 84.632(13)°$, $\gamma = 74.993(13)°$, $V = 1596.0(9)$ Å$^3$, $Z = 1$, $T = 200(2)$ K, $D_{calcd} = 1.853$ g cm$^{-3}$, 13853 reflections measured, 7218 independent ($R_{int} = 0.0689$), $R1 = 0.040$ ($I > 2\sigma(I)$), $wR2 = 0.101$ (all data). CCDC = 886212.

8 A similar reaction of 2-(4-dimethylaminophenyl)benzothiazoline with a mixture of silver(I) perchlorate and tetraacetonitrilecopper(I) perchlorate also gave a complex mixture, which is much more complicated than that formed from chloro(tetrahydrothiophene)-gold(I) and tetraacetonitrilecopper(I) perchlorate.

9 Anal. Calcd for **2**: C, 56.49; H, 4.74; N, 8.78%. Found: C, 56.71; H, 4.87; N, 8.71%.

10 Compound **2** was soluble in $CH_2Cl_2$ only slightly, and its solution color changed from orange to dark brown within several hours. The spectrum of the brown solution was identical with that of $[Cu_8(L)_8]^+$.

11 Crystal data for $\mathbf{2}\cdot C_7H_8$, Trigonal, $I4_1/a$, $a = 18.98(3)$ Å, $b = 18.98(3)$ Å, $c = 21.08(3)$ Å, $V = 7589(20)$ Å$^3$, $Z = 4$, $T = 200(2)$ K, $D_{calcd} = 1.255$ g cm$^{-3}$, 9923 reflections measured, 3003 independent ($R_{int} = 0.109$), $R1 = 0.085$ ($I > 2\sigma(I)$), $wR2 = 0.299$ (all data). CCDC = 886213.

12 The intense band is assignable as arising from $\pi$–$\pi^*$ transition within the conjugated 4-$NMe_2$–Ph–C(H)=N moiety.[3b]

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