

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

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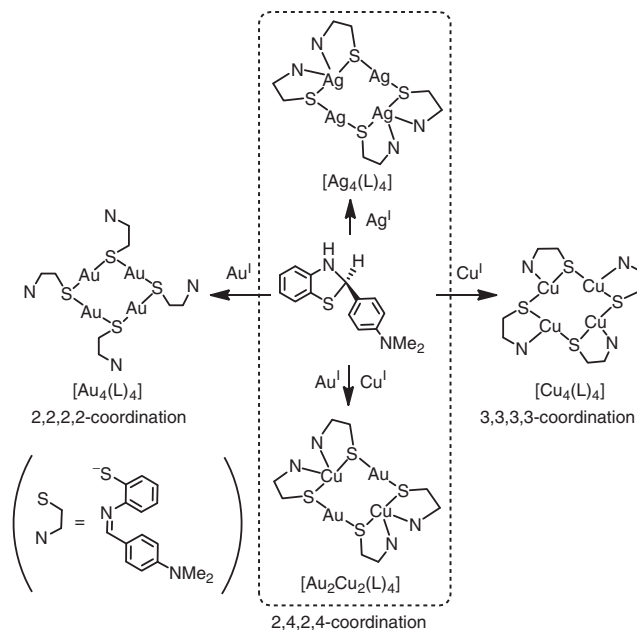
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A thiolato-bridged $\text{Au}^{\text{I}}_2\text{Cu}^{\text{I}}_2$ metalloring compound, $[\text{Au}_2\text{Cu}_2(\text{L})_4]$ ($\text{L} = (\text{C}_6\text{H}_4\text{NMe}_2)\text{CH}=\text{N}(\text{C}_6\text{H}_4\text{S}^-)$), together with an analogous Cu^{I}_4 compound, $[\text{Cu}_4(\text{L})_4]$, was newly prepared from 2-(4-dimethylaminophenyl)benzothiazoline. The $\text{Au}^{\text{I}}_2\text{Cu}^{\text{I}}_2$ compound was found to show structural and spectroscopic features comparable well with those of $[\text{Ag}_4(\text{L})_4]$, rather than those of $[\text{Au}_4(\text{L})_4]$ and $[\text{Cu}_4(\text{L})_4]$.

There has been considerable research interest in multi-nuclear 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, $[\text{Au}_4(\text{L})_4]$ and $[\text{Ag}_4(\text{L})_4]$ ($\text{L} = (\text{C}_6\text{H}_4\text{NMe}_2)\text{CH}=\text{N}(\text{C}_6\text{H}_4\text{S}^-)$), 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, $[\text{Au}_2\text{Ag}_2(\text{L})_4]$, 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, $[\text{Au}_2\text{Cu}_2(\text{L})_4]$. The preparation of an analogous Cu^{I}_4 complex, $[\text{Cu}_4(\text{L})_4]$, from 2-(4-dimethylaminophenyl)benzothiazoline is also reported. Notably, $[\text{Au}_2\text{Cu}_2(\text{L})_4]$ was found to exhibit structural and spectroscopic features that are comparable well with those of $[\text{Ag}_4(\text{L})_4]$, rather than those of $[\text{Au}_4(\text{L})_4]$ and $[\text{Cu}_4(\text{L})_4]$ (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 $\text{Au}^{\text{I}}_2\text{Cu}^{\text{I}}_2$ 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 ($1 \cdot 2\text{CHCl}_3$) 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 ($\text{L} = (\text{C}_6\text{H}_4\text{NMe}_2)\text{CH}=\text{N}(\text{C}_6\text{H}_4\text{S}^-)$) 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 $\text{Au}^{\text{I}}_2\text{Cu}^{\text{I}}_2$ metalloring structure with a C_2 symmetry. Each L ligand adopts a $\mu_2\text{-}\kappa^1\text{S}:\kappa^2\text{N},\text{S}$ coordination mode, in which its imine group coordinates to a Cu^{I} atom (av $\text{Cu}-\text{N} = 2.16(5) \text{ \AA}$) and its thiolato group bridges Au^{I} and Cu^{I} atoms (av $\text{Au}-\text{S} = 2.295(18) \text{ \AA}$, $\text{Cu}-\text{S} = 2.31(3) \text{ \AA}$). As a result, two Cu^{I} atoms are situated in an N_2S_2 tetrahedral geometry ($\text{N}-\text{Cu}-\text{N} = 117.88(14)^\circ$, $\text{S}-\text{Cu}-\text{S} = 111.10(5)^\circ$), while two Au^{I} atoms are in an S_2 linear geometry ($\text{S}-\text{Au}-\text{S} = 176.44(4)^\circ$). 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

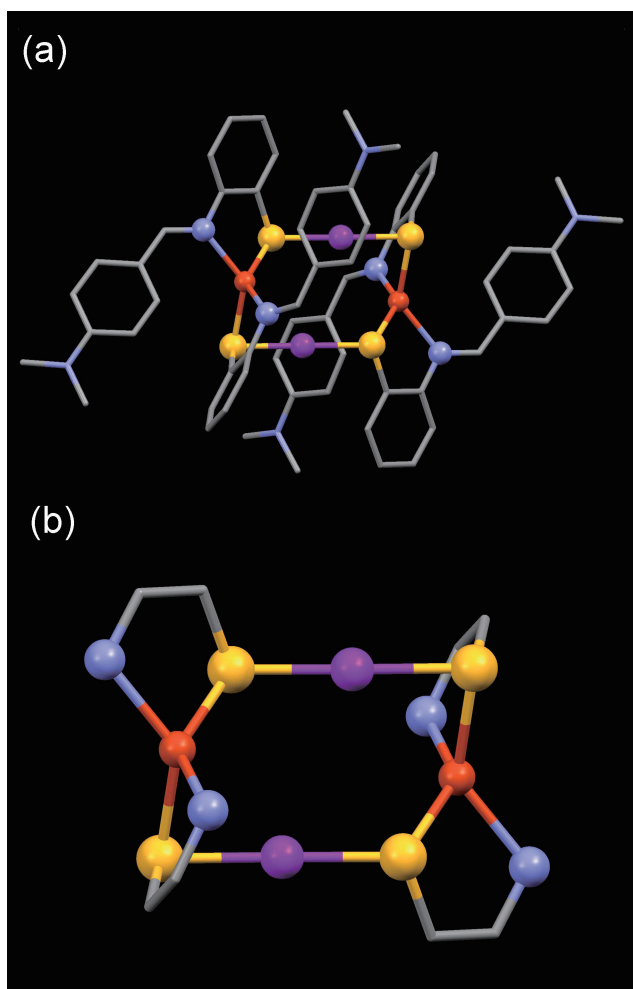


Figure 1. Perspective views of (a) **1** and (b) its core structure; Au^I: purple, Cu^I: brown, N: blue, S: yellow, C: gray. H atoms are omitted for clarity.

rather than to an Au^I center, accounts for the formation of this metalloring structure. Despite the C_i symmetric structure in crystal **1**, the ¹H NMR spectrum of **1** in CDCl₃ gave only a single set of signals for four L ligands (Figure S1a),⁵ suggestive of the flexible nature of its Au^I₂Cu^I₂S₄ metalloring framework with an averaged C_{2h} symmetry in solution.

It is possible that three heterometallic species, [Au₃Cu₁(L)₄], [Au₂Cu₂(L)₄], and [Au₁Cu₃(L)₄], besides two homometallic species, [Au₄(L)₄] and [Cu₄(L)₄], are formed from L ligands in combination with a 1:1 mixture of Au^I and Cu^I ions. In addition, two isomeric forms that are discriminated by the arrangement of Au^I and Cu^I ions, AuAuCuCu-type and AuCuAuCu-type, are possible for [Au₂Cu₂(L)₄]. However, the present reaction exclusively produced [Au₂Cu₂(L)₄] with an AuCuAuCu-type arrangement in a moderate yield of ca. 50%. Since the ¹H 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 CDCl₃/CD₃CN 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 [Au₂Ag₂(L)₄] with an AuAgAuAg-type arrangement is selectively formed in solution.^{4,8} The affinity of an imine group to a Cu^I center, which is much higher than to an 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 Cu^I₄ 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 [Cu₄(L)₄] but produced a brown compound of [Cu₈(L)₈](ClO₄) 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 [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 Cu^I₄ 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 [Cu₈(L)₈]⁺ in solution. Each L ligand in **2** also adopts a μ_2 - κ^1 S: κ^2 N,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 Cu^I atoms, and each Cu^I atom is situated in an NS₂ 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 Au^I₄ and Ag^I₄ compounds, [Au₄(L)₄] and [Ag₄(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 [Cu₄(L)₄] (**2**).⁴ However, in [Au₄(L)₄], all four Au^I atoms adopt a two-coordination geometry, whereas two of four Ag^I atoms adopt a two-coordination geometry and the other Ag^I atoms have a four-coordination geometry in [Ag₄(L)₄] (Figure S3).⁵ The 2,2,2,2-coordination in [Au₄(L)₄] and the 2,4,2,4-coordination in [Ag₄(L)₄] are both different from the 3,3,3,3-coordination found in **2**, in which four Cu^I atoms are unified to have a three-coordination geometry. It should be noted that the 2,4,2,4-coordination pattern in [Ag₄(L)₄] is the same as that in [Au₂Cu₂(L)₄] (**1**). In addition, the four bridging S atoms in [Ag₄(L)₄] are in an arrangement of parallelogram like in **1**, whereas those in [Au₄(L)₄] are in a square arrangement like in **2**. Thus, the overall metalloring structure in [Ag₄(L)₄] is well comparable with that in [Au₂Cu₂(L)₄] (**1**), rather than those in

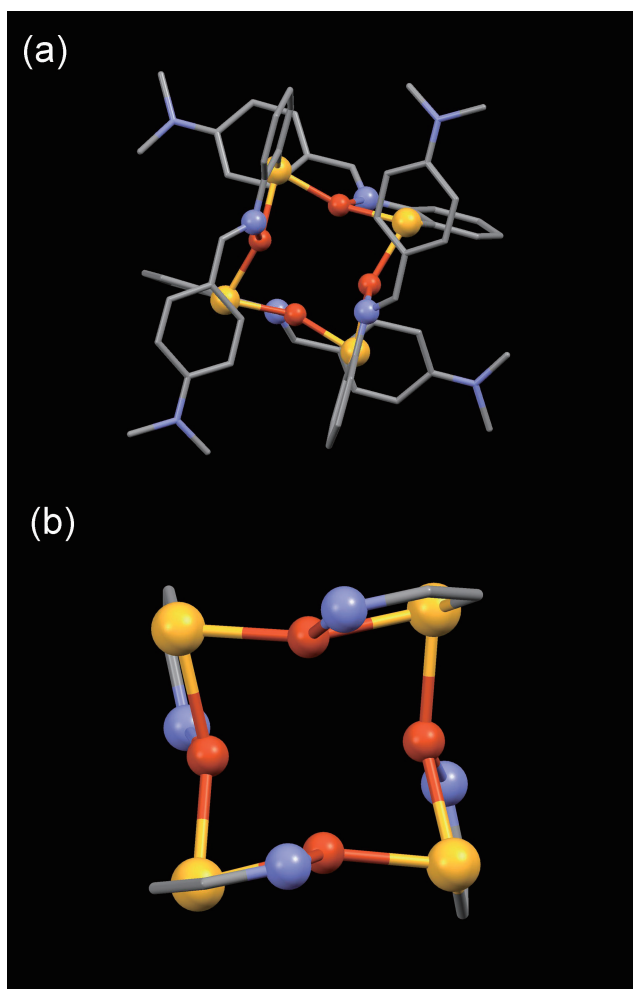


Figure 2. Perspective views of (a) **2** and (b) its core structure; Cu^I: brown, N: blue, S: yellow, C: gray. H atoms are omitted for clarity.

[Au₄(L)₄] and [Cu₄(L)₄] (**2**). Besides the structural feature, the similarity between [Ag₄(L)₄] and [Au₂Cu₂(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 [Ag₄(L)₄] (390 nm), rather than those for [Au₄(L)₄] (380 nm) and **2** (402 nm) (Figure S4).⁵

In summary, we showed that a single species of [Au₂-Cu₂(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 Cu₄ metal-oring compound, [Cu₄(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 [Au₂Cu₂(L)₄], as well as its electronic spectral feature, is similar to that of [Ag₄(L)₄], rather than those of [Au₄(L)₄] and [Cu₄(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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- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- Anal. Calcd for **1**·2CHCl₃: C, 41.81; H, 3.51; N, 6.29%. Found: C, 41.75; H, 3.51; N, 6.41%.
- Crystal data for **1**·2CHCl₃, Triclinic, *P* $\bar{1}$, *a* = 8.684(3) Å, *b* = 13.144(4) Å, *c* = 14.618(5) Å, α = 82.937(13)°, β = 84.632(13)°, γ = 74.993(13)°, *V* = 1596.0(9) Å³, *Z* = 1, *T* = 200(2) K, *D*_{calcd} = 1.853 g cm⁻³, 13853 reflections measured, 7218 independent (*R*_{int} = 0.0689), *R*₁ = 0.040 (*I* > 2σ(*I*)), *wR*₂ = 0.101 (all data). CCDC = 886212.
- 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.
- Anal. Calcd for **2**: C, 56.49; H, 4.74; N, 8.78%. Found: C, 56.71; H, 4.87; N, 8.71%.
- Compound **2** was soluble in CH₂Cl₂ 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 [Cu₈(L)₈]⁺.
- Crystal data for **2**·C₇H₈, Trigonal, *I*_{41/a}, *a* = 18.98(3) Å, *b* = 18.98(3) Å, *c* = 21.08(3) Å, *V* = 7589(20) Å³, *Z* = 4, *T* = 200(2) K, *D*_{calcd} = 1.255 g cm⁻³, 9923 reflections measured, 3003 independent (*R*_{int} = 0.109), *R*₁ = 0.085 (*I* > 2σ(*I*)), *wR*₂ = 0.299 (all data). CCDC = 886213.
- The intense band is assignable as arising from π–π* transition within the conjugated 4-NMe₂-Ph–C(H)=N moiety.^{3b}
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