

Synthesis and Characterization of Coinage Metal Aluminum Sulfur Species

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S Supporting Information

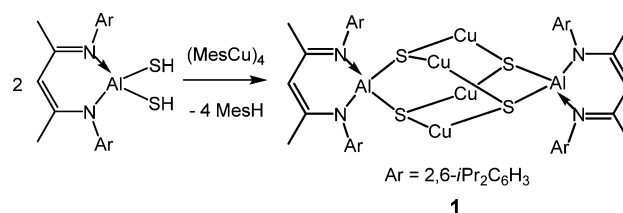
ABSTRACT: The synthesis of heterobimetallic cluster with the Al–S–M (M = Cu and Ag) structural unit has been realized for the first time by the reaction of aluminum-dithiol LAl(SH)₂ (L = HC[C(Me)N(Ar)]₂, Ar = 2,6-*i*Pr₂C₆H₃) with (MesCu)₄ and (MesAg)₄ (Mes = 2,4,6-Me₃C₆H₂), respectively. The isolated clusters exhibit core structures of Al₂Cu₄S₄ and Al₄Ag₈S₈, respectively. During the formation of the [LAl(SAg)₂]₄, a side product of LAlS₆ is formed. However, the reaction of LAl(SH)₂ with excess of sulfur and (MesAg)₄ resulted in the formation of LAlS₄ as the only product soluble in organic solvents. Both of them represent rare examples of aluminum polysulfides. All compounds were characterized by spectroscopic methods and single crystal X-ray diffraction studies.

In recent years organoaluminum chalcogenides have attracted great interest in the field of catalysis and chemical vapor deposition (CVD).¹ Al₂O₃ and aluminosilicates play a significant role as support, due to their high surface area, for metal catalysts.² To understand the basic intramolecular architecture of heterogeneous metal oxide catalysts, different aluminum-containing heterobimetallic oxides have been reported.³ However, their sulfur congeners are less known due to the limited synthetic precursors and methods, although the sulfur analogues might play an important role in desulfurization processes of crude oil and flue-gas. There are only a few examples known such as CpFe(CO)₂SPh(AlMe₃)⁴ and [Fe(CO)₃]₂S₂Al(η⁵-Cp*)⁵ complexes. Recently, we prepared {LAl(SH)[SLi(thf)₂]₂ and [{LAl(SLi)₂(thf)₃]}₂·2THF (L = HC[C(Me)N(Ar)]₂, Ar = 2,6-*i*Pr₂C₆H₃)⁶ as precursors for the preparation of organometallic sulfides. Some aluminum sulfur complexes including L₂Al₂Ge₄Li₂S₇,^{7a} LAl(μ-S)₂MCp₂ (M = Ti, Zr),⁶ LAl(μ-S)₂MR₂ (M = Ge, Sn; R = Ph, Me), and LAl(μ-S)₂M(μ-S)₂AlL (M = Ge, Sn)^{7b,c} were synthesized. However, to the best of our knowledge, complexes including the Al–S–M (M = Cu, Ag) unit have not been reported. In comparison to the synthesis of metal siloxanes⁸ and alumoxanes,³ heterobimetallic complexes mentioned above are mostly prepared by lithium aluminum thiolates instead of using their thiols. Therefore, we were interested in the preparation of heterobimetallic complexes directly from aluminum-dithiol. Herein, we report on the synthesis of heterobimetallic cluster [LAl(SM)₂]_n (M = Cu, n =

2; M = Ag, n = 4) by the reaction of LAl(SH)₂⁹ with (CuMes)₄¹⁰ and (AgMes)₄,¹¹ respectively.

The reaction of β-diketiminato aluminum-dithiol LAl(SH)₂ (L = HC[C(Me)N(Ar)]₂, Ar = 2,6-*i*Pr₂C₆H₃) with (MesCu)₄ in a 2:1 molar ratio was carried out in toluene in the temperature range from –20 °C to room temperature (Scheme 1). After

Scheme 1. Preparation of Compound 1



removal of all volatiles and extraction of the residue with *n*-hexane, colorless crystalline solid [LAl(SCu)₂]₂ (**1**) was obtained in a yield of 73%. This compound is air and moisture sensitive and thermally stable (235 °C (dec.)). Compound **1** was characterized by ¹H, ¹³C, and ²⁷Al NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The ¹H spectrum of **1** shows the characteristic septet (δ 3.56 ppm) and doublet resonances (δ 1.05 and 1.62 ppm) for the CHMe₂ and CHMe₂ of the L ligand backbone. No resonances for Mes group and SH are observed, which implies the elimination of all Mes groups. In the ¹³C NMR spectrum of **1**, a singlet at δ 97.97 ppm corresponds to the γ-C of the backbone, which is slightly high-field shifted when compared with that of LAl(SH)₂ (δ 98.70 ppm).

The structure of [LAl(SCu)₂]₂ (**1**) was further confirmed by X-ray single crystal diffraction. Compound **1** crystallizes in the monoclinic space group *P2*/*c*, which contains an Al₂Cu₄S₄ core (Figure 1). Both the planes defined by AlS₂ are perpendicular to each other and are perpendicular to the Cu₄ plane, respectively. This arrangement is quite different from the planar framework of copper siloxanes reported before.¹² The Al–S bond length (2.243(15) and 2.246(14) Å) in **1** is slightly longer than those in [κ³-S,O,O-LAl(SLi)(μ-O)P(OEt)₂]₂ (2.124(1) Å), [κ²-S,P-LAl(S)(μ-O)P(OEt)₂]₂Zn] (2.160(1) Å),¹³ [LAl(μ-S)₂TiCp₂] (2.208(1) and 2.197(1) Å),⁶ [LAl(μ-S)₂Ge₂]₂(μ-S)₃Li₂(thf)₂] (2.238(3) and 2.221(4) Å),^{7a} and LAl(μ-S)₂AlL (2.237(1) and 2.245(1) Å).^{7d} The Cu–S bond length (av 2.188 Å) is

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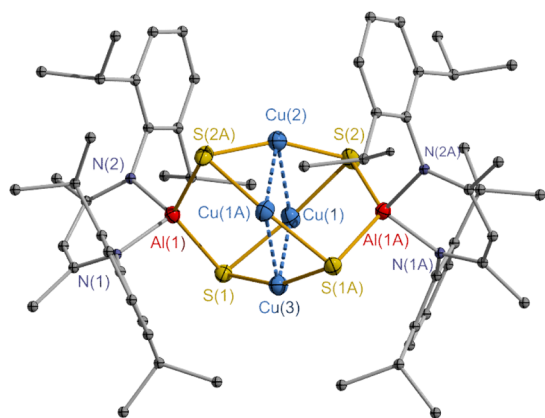
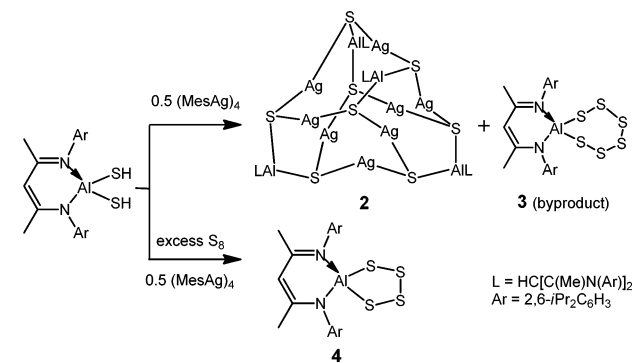


Figure 1. Molecular structure of **1** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

comparable to those in copper(III) 1,2-dicarbomethoxy-1,2-dithiolate (2.167(15)–2.183(12) Å).¹⁴ The short Cu(I)⋯Cu(I) separations (2.505(8)–2.547(8) Å) in **1** suggest the presence of attractive $d^{10}\cdots d^{10}$ interactions, similar to those in the cage compound $[\text{RSi}(\text{OCu})_3]_8$ ($\text{R} = (2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{SiMe}_3)$).¹⁵

Furthermore, we investigated the reaction of $\text{LAl}(\text{SH})_2$ with $(\text{MesAg})_4$. When carrying out the reaction under similar conditions as those for the synthesis of **1**, we obtained pure $[\text{LAl}(\text{SAg})_2]_4$ (**2**) as an off-white solid in moderate yield (55%) (Scheme 2). Compound **2** is soluble in toluene and THF, but

Scheme 2. Preparation of Compounds **2**, **3**, and **4**



only slightly soluble in *n*-hexane. Compound **2** is thermally stable and decomposes at 238 °C. The ¹H NMR spectrum of **2** shows characteristic resonances of the backbone of the β -diketiminato ligand. Two singlets (δ 1.36 and 1.46 ppm) are observed, which correspond to the β -Me groups, exhibiting a resonance mode quite different from those in compounds $\text{LAl}(\text{SH})_2$ (δ 1.51 ppm) and **1** (δ 1.57 ppm).

To obtain more insight into the structure of **2**, an X-ray single crystal diffraction study was carried out (see Supporting Information (SI)). The structural analysis clearly reveals the formation of an asymmetrically arranged tetrameric complex consisting of an $\text{Al}_4\text{Ag}_8\text{S}_8$ core (Figure 2). Compound **2** represents the first complex containing silver, aluminum, and sulfur as core elements. All S atoms are bound to two Ag atoms and weak $d^{10}\cdots d^{10}$ contacts between Ag atoms could be observed ($\text{Ag}(\text{I})\cdots\text{Ag}(\text{I})$ 2.806(11)–3.061(11) Å).¹⁶ The eight Ag atoms form a highly asymmetric core, which is quite different from that in **1** (see SI). The connecting line of Ag(3)–Ag(4) and that of Ag(2)–Ag(7) are nearly orthogonal to each other (87.55°) (see

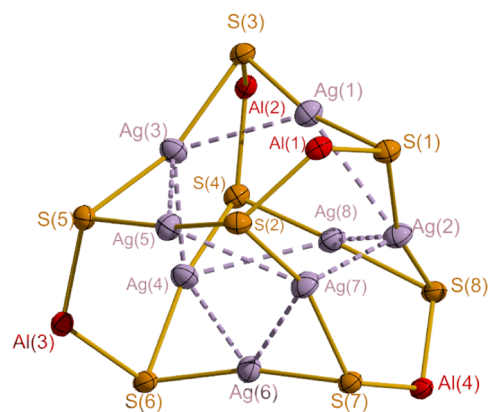


Figure 2. $\text{Al}_4\text{Ag}_8\text{S}_8$ core structure of **2** with thermal ellipsoids at 50% probability level. The ligands (L) are omitted for clarity.

SI, Figure S2). Such a structural motif could only be observed in some silver nanoparticles.¹⁷ The Ag–S bond lengths in **2** (2.365–2.435 Å) fall in the range of those observed in $[\text{AgSCH}(\text{SiMe}_3)_2]_8$ (2.387(4)–2.418(4) Å),¹⁸ $[\text{Ag}_4(\text{Phhexim})_2]\cdot\text{DMF}$ (2.402(7)–2.558(7) Å),¹⁹ $[\text{Ag}_2\{\text{Ag}(\text{MeSNS})\}_3][\text{PF}_6^-]_2$ (2.373(3)–2.489(3) Å), and $[\text{Ag}(\text{EtSNS})]_2[\text{AgOTf}]_2$ (SNS = $\text{NC}(\text{S})\text{-PPh}_2\text{NPPh}_2\text{C}(\text{S})\text{N}$) (2.399(2)–2.416(2) Å).²⁰

The LAlS_6 (**3**) was isolated as a byproduct in low yield in the reaction of $\text{LAl}(\text{SH})_2$ with $(\text{MesAg})_4$ (Scheme 2). It is a rare example of group 13 polysulfides. Al–S ion clusters with one aluminum atom in the sulfur ring have only been identified by mass spectrometry,²¹ and neutral Al–S clusters are studied by theoretical calculations.²² In the ²⁷Al NMR spectrum of **3**, one singlet at δ 121.65 ppm corresponds to the Al center coordinated by the ligand (L) and the S_6 unit. The X-ray single crystal diffraction study gave further information for the structure of **3** (Figure 3). A S_6 polysulfide binds to the Al center to form an

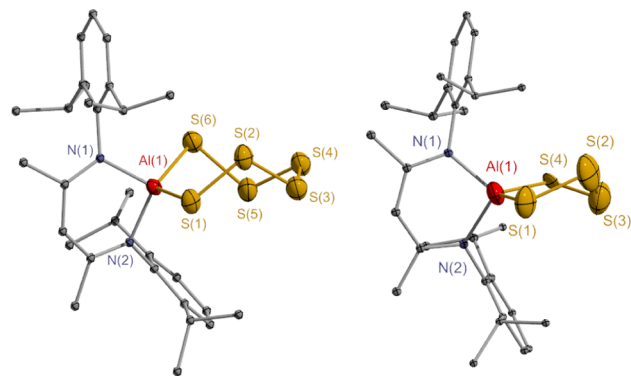


Figure 3. Molecular structures of **3** (left) and **4** (right) with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

aluminum AlS_6 seven-membered ring. The S–S bond length (av 2.01 Å) in **3** is shorter than that in S_8 (av 2.05 Å),²³ $\text{LAl}(\mu\text{-S}_3)_2\text{AlL}$ ($\text{L} = \text{HC}[\text{C}(\text{Me})\text{N}(\text{Ar})]_2$, $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$) (av 2.08 Å),²⁴ $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)(\mu\text{-S}_3)]_2$ (av 2.05 Å),²⁵ and $[(\eta^5\text{-MeC}_5\text{H}_4)\text{Ti}(\mu\text{-S}_3)]_2$ (av 2.06 Å).²⁶

The formation of **3** probably occurs due to the presence of residual sulfur during the preparation of $\text{LAl}(\text{SH})_2$. To confirm this assumption, additional elemental sulfur was added to the reaction mixture of $\text{LAl}(\text{SH})_2$ and $(\text{MesAg})_4$. At room temperature a black suspension was slowly formed. The black precipitate

proved to be Ag_2S by Raman spectroscopy (see SI). However, instead of the expected LAlS_6 (**3**), a new compound was obtained having the composition LAlS_4 (**4**), a new compound was obtained having the composition LAlS_4 (Scheme 2). Even when the amount of sulfur was increased, only compound **4** was formed. Obviously **4** is more stable than **3**, which has also been confirmed by theoretical studies.²² The ^1H spectrum of **4** exhibits characteristic resonances of the ligand backbone with one singlet (δ 1.56 ppm), one septet (δ 3.36 ppm), and two doublets (δ 1.09, 1.48 ppm). The ^{27}Al NMR spectrum of **4** exhibits a singlet (δ 133.18 ppm) for the Al center, which is slightly downfield shifted when compared with that in **3**. The X-ray single crystal structure of **4** shows the aluminum atom in the spiro center of the six- (AlC_3N_2) and five-membered (AlS_4) rings (Figure 3). The S–S bond length (av 2.07 Å) is longer than that of **3** (av 2.01 Å) and comparable to those of the related compounds mentioned above.^{23–26}

In summary, the aluminum sulfur derivatives $[\text{LAl}(\text{SCu})_2]_2$ (**1**), $[\text{LAl}(\text{SAG})_2]_4$ (**2**), LAlS_6 (**3**), and LAlS_4 (**4**) were prepared. Compounds **1** and **2** are the first examples of the coinage metals containing aluminum and sulfur. Both of them showed during the preparation the complete elimination of the Mes groups from the metal precursors and formed new hexanuclear or dodecanuclear heterobimetallic species. In addition, the byproduct LAlS_6 (**3**) was isolated, which exhibits a new and stable aluminum polysulfide. When the same reaction was conducted with additional sulfur, only LAlS_4 was obtained as soluble product in organic solvents. Increasing the amount of sulfur had no influence on the reaction, which indicates that the AlS_4 complex is more stable than AlS_6 .

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed synthetic procedures, analytical and characterization data of **1–4**, the cif files of **1–4**, and the details of crystal structure refinements, fluorescence spectra of **1** and **2**, and Raman data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ Notes

The authors declare no competing financial interest.

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