

Bridging of Trigoldsulfonium Clusters by a Silver(I) Ion

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Z. Naturforsch. **52b**, 301–303 (1997);
received January 3, 1997

Gold Clusters, Silver Bridging, Sulfonium Cations, Mixed Gold/Silver Cluster

Treatment of tris[(triphenylphosphine)gold(I)]sulfonium tetrafluoroborate with AgBF_4 (molar ratio 2:1) in tetrahydrofuran affords a heptanuclear mixed-metal cluster trication $\{[(\text{Ph}_3\text{P})_6\text{Au}_6\text{AgS}_2](\text{thf})\}^{3+}$ as the tetrafluoroborate salt. The crystal structure of the compound has been determined by X-ray diffraction. The silver atom is found in a bridging position between the two Au_3S units with short contacts to both sulfur atoms and to three out of six gold atoms. The coordination sphere of the silver atom is complemented by a tetrahydrofuran molecule. In di(tri)chloromethane solutions there is rapid site exchange of the silver coordination as shown by virtual equivalence of the phosphine ligands on the NMR time scale at ambient temperature.

Introduction

Sulfide anions S^{2-} are efficient clustering centers for gold(I) cations. Depending on the stoichiometry of the reactions stable products with various S/Au ratios have been found, including monosulfur species of the type $[\text{S}(\text{AuL})_2]$, $[\text{S}(\text{AuL})_3]^+$ and $[\text{S}(\text{AuL})_4]^{2+}$ where the gold atoms carry stabilizing phosphine ligands L [1,2]. With a deficit of L, or in the absence of L, ring and cage anions are formed with intriguing compositions and structures like $[\text{S}_2\text{Au}(\text{AuL})_4]^+$, $[\text{AuS}_9]^-$, $[\text{Au}_2\text{S}_8]^{2-}$, or $[\text{Au}_{12}\text{S}_8]^{4+}$ [3–6].

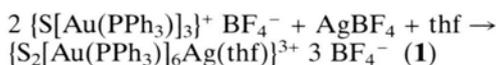
In these series the successful build-up of a gold cluster with more than three sulfur atoms at a given sulfur center to give dications $[\text{S}(\text{AuL})_4]^{2+}$ is an indication that sulfonium cations $[\text{S}(\text{AuL})_3]^+$ are still susceptible to electrophilic attack by additional cations $[\text{LAu}]^+$ or naked $[\text{Au}]^+$. The products do not have sulfur-centered tetrahedral structures, but were found to be square pyramidal

with distorted squares or rectangles of gold atoms. The short Au–Au edges of these units suggest stabilizing metal-metal bonding for these moieties and their aggregates [1,7].

In the present short note we report the addition of $[\text{Ag}]^+$ cations to $[\text{S}(\text{Au}(\text{PPh}_3))_3]^+$ cations, which leads to a heptanuclear mixed-metal cluster.

Results

Treatment of a solution of tris[(triphenylphosphine)gold(I)]sulfonium tetrafluoroborate [8] in dichloromethane with a solution of silver tetrafluoroborate in tetrahydrofuran (molar ratio of the reactants: 2:1) at 20 °C gives good yields (61%) of a colourless solid product upon precipitation by addition of diethylether to the reaction mixture. The compound is soluble in di- or trichloromethane, but insoluble in pentane or diethylether. The solid is stable to air and moisture, but the solutions undergo rapid decomposition.



The solutions of the product in CDCl_3 show one singlet signal in the ^{31}P $\{^1\text{H}\}$ NMR spectrum at 20 °C, indicating virtual equivalence of all ligands on the NMR time scale. Accordingly, the ^1H and ^{13}C $\{^1\text{H}\}$ spectra also have only one set of phenyl signals. These spectra also show the presence of a tetrahydrofuran solvate, which was later confirmed by elemental analysis and X-ray diffraction (below). The FD and FAB mass spectra exhibit the $[\text{S}(\text{AuL})_3]^+$ cation as the parent peak.

Crystals of compound **1** are monoclinic, space group C2/c, with $Z = 4$ formula units in the unit cell. The lattice is composed of independent trications and anions (ratio 1:3). The two tris[(triphenylphosphine)gold(I)]sulfonium components are related by a crystallographic center of inversion (Fig. 1). The silver atom is disordered over two positions which could be refined using a split model. The tetrahydrofuran is also distributed over two sites and was calculated as accompanying the silver atom in each of its two positions.

In both of the symmetry-related, equivalent positions the silver atom has close contacts with two sulfur atoms $[\text{AgS}/\text{AgS}']$ 2.668(4)/2.430(3) Å, and with three out of the six gold atoms $[\text{Au1}-\text{Ag}$ 2.852(2), $\text{Au2}-\text{Ag}$ 2.838(2), $\text{Au2}'-\text{Ag}$ 2.948(2) Å]. All these metal-metal distances are shorter than in the pure metals or their binary alloys. The overall geometry of the heterometallic SAu_3Ag pyramids

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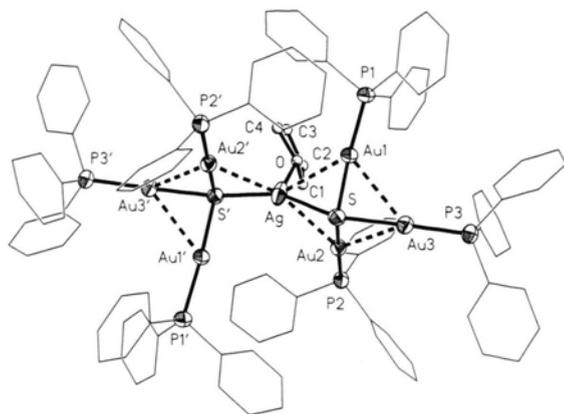


Fig. 1. Structure of the trication of compound **1** with atomic numbering. The molecule has a crystallographic center of inversion. The silver atom and the tetrahydrofuran molecule are disordered over two positions related by the center of inversion. Only one setting is shown with the corresponding connectivities. (ORTEP, 50% probability ellipsoids, except for the phenyl groups; hydrogen atoms omitted.) Selected bond lengths [Å]: Ag-S 2.668(4), Ag-S' 2.430(3), Ag-Au1 2.852(2), Ag-Au2 2.838(2), Ag-Au2' 2.948(2), Au1-S 2.321(3), Au2-S 2.335(3), Au3-S 2.373(3), Au1-Au3 3.1097(7), Au2-Au3 3.0015(7), Ag-O 2.53(2).

is similar to that of the homometallic counterpart SAu₄ in the corresponding dications [7]. The two units are sharing the silver atom as a common vertex. The basic structure of the two SAu₃ pyramids is not changed significantly by the addition of the silver atom [8], and Au–Au distances between 3.0015(7) and 3.1097(7) Å are retained, which correspond to Au–S–Au angles as small as 79.21(9) – 82.97(9)°.

The tetrahydrofuran molecule shows the standard envelop conformation, and its oxygen atom has an O–Ag contact of 2.53(2) Å. The triphenylphosphine units show no anomalies. Further details of the structure determination and its results are summarized in the Experimental Part and have been deposited.

Experimental Part

All experiments were routinely carried out under dry, purified nitrogen. Standard equipment was used throughout. The sulfonium salt was prepared following published procedures [8].

Preparation: [S(AuPPh₃)₃]BF₄ (0.19 g, 0.13 mmol) is dissolved in CH₂Cl₂ (10 ml) and treated with a solution of AgBF₄ (0.013 g, 0.064 mmol) in C₄H₈O (2 ml) at 20 °C with stirring. After 1 h the

solution is concentrated in a vacuum and layered with diethylether to precipitate the product. Colorless crystals are collected after 3 d (0.26 g, 61% yield).

C₁₀₈H₉₀AgAu₆B₃F₁₂P₆S₂ · C₄H₈O (3260.05)
 Calcd. C 41.26 H 3.03 Au 36.25 Ag 3.31%,
 Found C 40.56 H 3.05 Au 36.00 Ag 3.30%.

MS (FD / FAB): *m/z* = 1408 (100%/35%),
 [S(AuPPh₃)₃]⁺.

NMR (CDCl₃, 20 °C): ³¹P{¹H}, δ 33.04, s; ¹H, 1.83 (m, CH₂, thf), 3.72 (m, CH₂, thf), 7.20–7.50 (m, Ph); ¹³C{¹H}, 25.6 (s, CH₂, thf), 68.0 (s, CH₂, thf), 127.7 (d, J 60.1 Hz, Ph-C1), 129.6 (d, J 11.9 Hz, Ph-C3), 132.5 (s, Ph-C4), 133.8 (d, J 13.3 Hz, Ph-C2).

Structure determination

A specimen of suitable quality was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection. During data collection three standard reflections were measured periodically as a general check of crystal and instrument stability. Lp correction was applied and intensity data were corrected for absorption effects (psi-scans, $\mu(\text{Mo-K}\alpha) = 80.50 \text{ cm}^{-1}$, $T_{\text{min}}/T_{\text{max}} = 0.672/1.000$). The structure was solved by Patterson methods and completed by full-matrix least-squares techniques against F². All non-H atoms except for those of one disordered BF₄ anion and those of the solvent thf molecule were refined with anisotropic displacement parameters. All H-atoms were placed in idealized calculated positions and allowed to ride on their carbon atoms with $U_{\text{iso}}(\text{fix}) = 1.5 \times U_{\text{eq}}(\text{C})$.

Crystal data: C₁₀₈H₉₀AgAu₆B₃F₁₂P₆S₂ · C₄H₈O, $M_r = 3259.94$, colorless crystals of dimensions 0.1 × 0.13 × 0.6 mm, monoclinic, $a = 24.853(3)$, $b = 18.828(2)$, $c = 24.347(3)$ Å, $\beta = 91.70(1)^\circ$, space group C2/c, $Z = 4$, $V = 11401.76 \text{ \AA}^3$, $D_{\text{calc}} = 1.901 \text{ g cm}^{-3}$, $F(000) = 6176$; Enraf Nonius CAD4 diffractometer, Mo-K α radiation ($\lambda = 0.71073$), $T = -62$ °C. From 9984 measured [$(\sin\theta/\lambda)_{\text{max}} = 0.64 \text{ \AA}^{-1}$] and 9769 unique reflections ($R_{\text{int}} = 0.028$) 7664 were used for refinement. The structure converged for 580 refined parameters to an $R(wR2)$ value of 0.0532 (0.1299). Residual electron densities: +3.17/–2.72 eÅ^{–3}.

Further information on the X-ray structure determination can be obtained from Fachinformati-onszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD 406335, the names of the authors, and the journal citation.

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