in other Au^{III} ylide complexes (2.04–2.16 Å).[7] The P–C(methylene) and P–C(phenyl) distances are also within expected ranges, with average lengths of 1.771 (5) and 1.805 (6) Å, respectively.

The geometry of **1** is composed of essentially planar units involving a 1,2-benzenedithiolate ligand, a gold atom, and two methylene carbon atoms. The ylide ligands and the planar $Au(S_2C_6H_4)$ units form a stair step molecule with a geometry that gives excellent crystal packing. The pseudochair conformation of the central eight-membered ring allows this stair step arrangement and as a result separates the two metal atoms to a distance of 4.40 Å. Conversely, a boat conformation around the eight-membered ring with the same cis,cis geometry would place the square-planar metal atoms on top of each other and give a metal–metal separation of ~3.1 Å, a distance commonly seen in trans,trans geometries of Au^{III} ylide dimers.

The 1,2-dithiolate ligand in complex **1** chelates the gold atoms. The preference for a chelating coordination by 1,2-dithiolate ligands is well-known, especially[16] for Au^{III}. The achievement of such a coordination arrangement probably contributes significantly to the formation of the observed cis,cis geometry. The Au–S bond distances of 2.317 (2) and 2.322 (1) Å are shorter than Au–S distances observed in a series of Au^{II} ylide dimers,[10] where the distances average ~2.40 Å. The observed distances are similar, however, to Au–S distances observed in monomeric Au^{III} compounds containing thiolates.[16]

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Supplementary Material Available: Listings of crystal data, thermal parameters, and hydrogen coordinates (4 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

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Gold Thiolate Complexes with Short Intermolecular Au–Au Distances from Reactions of Organic Disulfides with Gold(I) Complexes. Syntheses and Crystal Structures of $[Au^{I}_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$ and $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$

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The reaction of $PhCH_2SSCH_2Ph$ or $Na(SCH_2Ph)$ with $Au(PPh_3)NO_3$ in CH_2Cl_2 yields the dinuclear compound $[Au^{I}_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$ (**1**). The reaction of PhSSPh with Au(CO)Cl in CH_2Cl_2 yields the dinuclear compound $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$ (**2**). The crystal structures of **1** and **2** have been determined by single-crystal X-ray diffraction analysis. Compound **1** dimerizes in the solid to form a tetranuclear cluster with intermolecular Au–Au separations of 3.077 (2) and 3.194 (2) Å. Compound **2** also dimerizes through the eclipse of two square-planar Au^{III} units with an Au^{III}–Au^{III} separation of 3.416 (1) Å. **1** crystallizes in a monoclinic space group $P2_1/n$ with $a = 17.743$ (6) Å, $b = 27.03$ (1) Å, $c = 17.926$ (4) Å, $\beta = 95.29$ (2)°, $V = 8560$ (5) $Å^3$, and $z = 4$. Refinement using 4131 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ gave $R = 0.078$ and $R_w = 0.0881$. **2** crystallizes in a triclinic space group $P1$ with $a = 7.435$ (2) Å, $b = 10.046$ (2) Å, $c = 12.611$ (3) Å, $\alpha = 85.02$ (2)°, $\beta = 88.81$ (2)°, $\gamma = 69.68$ (2)°, $V = 880.0$ (4) $Å^3$, and $Z = 2$. Refinement using 1670 reflections with $F_o^2 \geq 3\sigma(F_o^2)$ yielded $R = 0.0498$ and $R_w = 0.0658$.

Introduction

Chemists have been fascinated by the potential importance of gold(I) compounds as antiarthritis medicine. Gold(I) compounds with phosphine ligands or sulfur-containing ligands are most commonly used in the treatment of arthritis. However, very little is known about how gold compounds perform their functions in vivo, despite the fact that numerous studies have been carried out in this area.[1] Some studies suggest that the interactions of the Au^{I} center with thiol or disulfide linkages in biomolecules may play an important role. An important paper by Shaw et al.[1e] has appeared very recently. For these reasons we have been interested in the reactions of organic disulfides or polysulfides with gold(I) complexes, since such reactions may not only produce new gold thiolate compounds with the potential use in medicine but also provide information on the possible function of Au^{I} compounds in biological systems. Organic disulfides and polysulfides have been found to undergo oxidative addition reactions[2a,b,d] with ylide gold(I) dimers to form metal–metal-bonded gold(II) species.[2] Reactions of organic disulfides with monomeric gold(I) complexes have been described.[1e,2c] In this paper, we describe the syntheses and crystal structures of two new thiolate gold compounds, $[Au^{I}_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$ (**1**) and $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$ (**2**), obtained from the reactions of $PhCH_2SSCH_2Ph$ and PhSSPh with $Au(PPh_3)NO_3$ and Au(CO)Cl, respectively.

Experimental Section

All reactions were carried out under an N_2 atmosphere. All solvents were freshly dried before use. Au(CO)Cl and $Au(PPh_3)NO_3$ were prepared according to the literature.[3] ^1H NMR spectra were taken on a Varian XL-200 spectrometer at 200 MHz. Elemental analyses were done by Desert Analytics Co., Tucson, AZ.

Synthesis of $[Au_2(PPh_3)_2(\mu\text{-}SCH_2Ph)]NO_3$ (1). (a) A 10-mg sample of $Au(PPh_3)NO_3$ (0.019 mmol) was dissolved in 3 mL of CH_2Cl_2, and 5 mg of $PhCH_2SSCH_2Ph$ (0.020 mmol) was added to the solution. After the mixture was stirred for 1 h, the solution was concentrated to 1 mL in vacuo. A 1-mL aliquot of diethyl ether was added. After a few days of standing at 0 °C, colorless crystals of **1** precipitated from the solution.

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Table I. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{86}H_{74}N_2O_6P_4S_2Au_4 \cdot CH_2Cl_2$	$C_{12}H_{10}Cl_4S_2Au_2$
fw	2292.36	754.08
space group	$P2_1/n$	$P\bar{1}$
a, Å	17.743 (6)	7.435 (2)
b, Å	27.03 (1)	10.046 (2)
c, Å	17.926 (4)	12.611 (3)
α, deg	90	85.02 (2)
β, deg	95.29 (2)	88.81 (2)
γ, deg	90	69.68 (2)
V, Å^3	8560 (5)	880.4 (5)
Z	4	2
d_{calc}, g cm^{-3}	1.79	2.84
μ(Mo Kα), cm^{-1}	72.5	178.9
radiation λ(Mo Kα), Å	0.71069	
T, °C	22	
transm coeff: max, min	0.747, 0.513	0.727, 0.404
R^a	0.0787	0.0498
$R_w{}^b$	0.0881	0.0658

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum/w(|F_o| - |F_c|)]/\sum\sqrt{w}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + |g|F_o{}^2]$.

(b) A 32-mg sample of $Au(PPh_3)NO_3$ (0.061 mmol) was dissolved in 5 mL of CH_2Cl_2, and 4 mg of $NaSCH_2Ph$ (0.027 mmol) was added. The mixture was stirred for 2 h at 22 °C. After filtration, a light yellow solution was obtained. Excess diethyl ether was added. Crystallization at 0 °C yielded crystals of **1** (10 mg, 29% yield). Anal. Calcd for $C_{86}H_{74}N_2O_6P_4S_2Au_4 \cdot CH_2Cl_2$: C, 45.58; H, 3.34; N, 1.22. Found: C, 44.95; H, 3.30; N, 1.10. ^{1}H NMR ($CDCl_3$, δ): 4.53 (s, $-CH_2$), 7.25–7.65 (m, $-C_6H_5$).

Synthesis of $Au_2Cl_4(\mu\text{-}SPh)_2$ (2). To a CH_2Cl_2 solution of excess PhSSPh (50 mg, 0.23 mmol) was added Au(CO)Cl (40 mg, 0.15 mmol) at 22 °C. The solution became orange rapidly. After 4 h of stirring, a red solution was obtained. This solution was filtered. Crystallization from CH_2Cl_2/hexane produced red crystals of **2** in good yield. The reaction presumably is described by the equation 2Au(CO)Cl + PhSSPh → **2** + 2CO + other products. Anal. Calcd for $C_{12}H_{10}Cl_4S_2Au_2$: C, 19.11; H, 1.34. Found: C, 18.70; H, 1.16.

X-ray Crystals Structures. Colorless crystals of **1** suitable for X-ray diffraction analysis were grown from CH_2Cl_2/hexane at 0 °C. Red crystals of **2** for X-ray diffraction analysis were obtained by crystallization from CH_2Cl_2/hexane at 0 °C.

Crystals were mounted on glass fibers and sealed with epoxy. Unit cell constants were determined from 25 machine-centered reflections. Data were collected on a Nicolet R3m/E diffractometer controlled by a Data General Nova 4 minicomputer using graphite-monochromated Mo Kα radiation at ambient temperature. Data in the range $4° \le 2\theta \le 45°$ ($h \le 20$, $k \le 30$, $|l| \le 20$) were collected for **1**. Data in the range $4° \le 2\theta \le 44°$ ($-8 \le h \le 0$, $|k| \le 11$, $|l| \le 14$) were collected for **2**. At the end of data collection for **1** the crystal decayed by about 30%. All data were corrected for decay and Lorentz and polarization effects. Empirical absorption corrections were applied for both crystals. Data processing was performed on a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic software (version 5.1). Scattering factors including terms for anomalous dispersion were taken from ref 4.

The crystal of **1** belongs to monoclinic crystal systems. The space group $P2_1/n$ for **1** was uniquely determined by systematic absences. The crystal of **2** belongs to triclinic crystal systems. Crystals of **1** were solvated by a CH_2Cl_2 molecule (one molecule of CH_2Cl_2 per molecule of **1**). Unfortunately, this solvent molecule was not located and refined successfully. The two NO_3^- groups and the phenyl group bonded to C(2) are disordered in the lattice. Although data were collected twice for **1** despite the large quantities of unique reflections, the disorder problems for NO_3^- groups were not resolved due to the quality of the crystals and decay. Two sets of phenyl groups bonded to C(2) were located. Each set was refined with 54% and 46% occupancies, respectively. The C(226) atom in the second set of the phenyl group has a very small thermal parameter and was not refined well apparently due to the disorder. The positions of metal atoms in **1** were determined by direct methods, while the positions of metals atoms in **2** were determined by heavy-atom methods. All non-hydrogen atoms were located by subsequent difference Fourier syntheses. Metal, S, and P atoms in **1** were refined anisotropically. All non-hydrogen atoms in **2** were refined anisotropically. Phenyl rings were refined as rigid bodies with a fixed C–C distance, 1.395 Å, and C–C–C angle, 120°. The positions of hydrogen atoms on the phenyl rings were calculated by using a fixed C–H bond length, 0.96 Å. Their contributions were included in the structure factor calculations. The largest peak in the final difference Fourier map of **1**, 1.86 e/Å^3, is at 1.14 Å from Au(2). The largest peak in the final difference Fourier map of **2**, 1.37 e/Å^3, is at 1.37 Å from Cl(2). The data of crystallographic analyses are given in Table I.

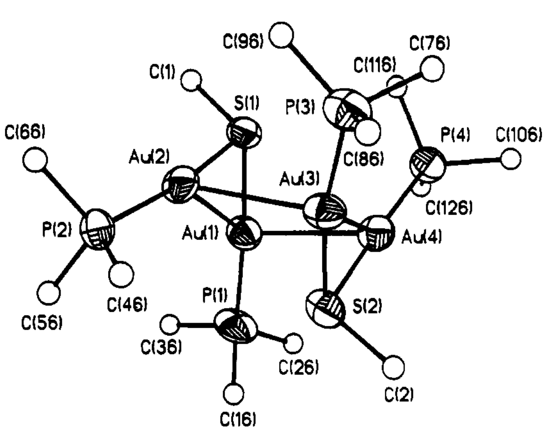

Figure 1. Dicationic structure of **1** showing 50% thermal ellipsoids and the labeling scheme. Phenyl groups are omitted from the drawing for clarity.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)^a for $[Au^I_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$ (**1**)

atom	x	y	z	$U_{iso}{}^b$
Au(1)	8815 (1)	1435 (1)	2724 (1)	60 (1)*
Au(2)	7917 (1)	797 (1)	3811 (1)	58 (1)*
Au(3)	6769 (1)	469 (1)	2421 (1)	58 (1)*
Au(4)	7865 (1)	949 (1)	1399 (1)	58 (1)*
P(1)	8728 (8)	2263 (4)	2509 (7)	83 (6)*
P(2)	7125 (7)	978 (4)	4706 (6)	62 (5)*
P(3)	6575 (7)	−359 (4)	2577 (6)	65 (5)*
P(4)	8750 (7)	574 (4)	738 (6)	61 (5)*
S(1)	8886 (7)	593 (4)	3059 (5)	59 (4)*
S(2)	6897 (7)	1293 (4)	2026 (6)	62 (5)*
C(1)	9773 (24)	488 (15)	3687 (22)	74 (13)
C(2)	6104 (25)	1398 (15)	1304 (23)	76 (14)
C(16)	7752 (17)	2491 (9)	2543 (13)	42 (10)
C(26)	8974 (15)	2466 (9)	1632 (20)	93 (16)
C(36)	9345 (21)	2573 (10)	3216 (16)	78 (14)
C(46)	6110 (16)	926 (9)	4492 (12)	60 (12)
C(56)	7271 (18)	1591 (12)	5047 (16)	73 (14)
C(66)	7337 (15)	584 (8)	5486 (15)	61 (12)
C(76)	6847 (14)	−677 (8)	1738 (16)	65 (13)
C(86)	5591 (16)	−510 (9)	2602 (13)	52 (11)
C(96)	7095 (15)	−656 (8)	3352 (13)	63 (13)
C(106)	8307 (13)	279 (10)	−96 (14)	67 (13)
C(116)	9241 (15)	103 (9)	1284 (14)	40 (10)
C(126)	9469 (16)	991 (11)	462 (15)	73 (13)

[a] Cf. Figure 1. The full listing is given in the supplementary materials. Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic U is defined as one-third of the trace of the U_{ij} tensor.

Results and Discussion

Synthesis and Crystal Structure of $[Au^I_2(PPh_3)_2(\mu\text{-}SCH_2Ph)]NO_3$ (1). Compound **1** was obtained as a major product initially from the reaction of $Au^I(PPh_3)NO_3$ with $PhCH_2SSCH_2Ph$ in CH_2Cl_2. The reaction mechanism has not been understood. The disulfide ligand probably was reduced by a Au^I center. This was supported by the observation of some yellow materials formed from the reaction, which could be Au^{III} compounds. Compound **1** can also be obtained by the reaction of $NaSCH_2Ph$ with 2 equiv of $Au(PPh_3)NO_3$ in CH_2Cl_2. When irradiated by UV light at 22 °C, **1** emits a red color in the solid state. **1** was fully characterized by ^{1}H NMR, elemental, and single-crystal X-ray diffraction analyses.

The structure of the cation in **1** is shown in Figure 1. Atomic positional and thermal parameters are given in Table II. Selected

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(4) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham: England, 1974; Vol. I (present distributor: D. Reidel, Dordrecht, The Netherlands).

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Au^I_2(PPh_3)_2(\mu\text{-}SCH_2Ph)](NO_3)$ (**1**)[a]

A. Bond Lengths			
Au(1)-Au(2)	3.142 (3)	Au(1)-Au(4)	3.077 (2)
Au(1)-P(1)	2.275 (11)	Au(1)-S(1)	2.354 (10)
Au(2)-Au(3)	3.194 (2)	Au(2)-P(2)	2.282 (12)
Au(2)-S(1)	2.346 (11)	Au(3)-Au(4)	3.077 (3)
Au(3)-P(3)	2.287 (11)	Au(3)-S(2)	2.353 (10)
Au(4)-P(4)	2.289 (12)	Au(4)-S(2)	2.331 (12)
P(1)-C(16)	1.844 (33)	P(1)-C(26)	1.759 (37)
P(1)-C(36)	1.805 (33)	P(2)-C(46)	1.810 (31)
P(2)-C(56)	1.778 (35)	P(2)-C(66)	1.769 (27)
P(3)-C(76)	1.834 (30)	P(3)-C(86)	1.799 (31)
P(3)-C(96)	1.786 (26)	P(4)-C(106)	1.809 (27)
P(4)-C(116)	1.783 (27)	P(4)-C(126)	1.805 (31)
S(1)-C(1)	1.870 (40)	S(2)-C(2)	1.843 (43)
C(1)-C(206)	1.522 (49)	C(2)-C(216)	1.488 (86)
C(2)-C(226)	1.333 (70)		
B. Bond Angles			
Au(2)-Au(1)-Au(4)	88.4 (1)	Au(2)-Au(1)-P(1)	127.9 (4)
Au(4)-Au(1)-P(1)	105.4 (3)	Au(2)-Au(1)-S(1)	47.9 (3)
Au(4)-Au(1)-S(1)	78.3 (2)	P(1)Au(1)-S(1)	174.8 (4)
Au(1)-Au(2)-Au(3)	89.5 (1)	Au(1)-Au(2)-P(2)	134.4 (3)
Au(3)-Au(2)-P(2)	102.6 (3)	Au(1)-Au(2)-S(1)	48.2 (2)
Au(3)-Au(2)-S(1)	86.3 (3)	P(2)-Au(2)-S(1)	170.4 (4)
Au(2)-Au(3)-Au(4)	87.4 (1)	Au(2)-Au(3)-P(3)	105.6 (3)
Au(4)-Au(3)-P(3)	126.6 (3)	Au(2)-Au(3)-S(2)	84.3 (3)
Au(4)-Au(3)-S(2)	48.6 (3)	P(3)-Au(3)-S(2)	169.4 (4)
Au(1)-Au(4)-Au(3)	93.0 (1)	Au(1)-Au(4)-P(4)	103.6 (3)
Au(3)-Au(4)-P(4)	128.5 (3)	Au(1)-Au(4)-S(2)	80.4 (3)
Au(3)-Au(4)-S(2)	49.3 (3)	P(4)-Au(4)-S(2)	175.8 (4)
Au(1)-P(1)-C(16)	111.9 (10)	Au(1)-P(1)-C(26)	116.1 (11)
C(16)-P(1)-C(26)	103.7 (13)	Au(1)-P(1)-C(36)	108.1 (11)
C(16)-P(1)-C(36)	109.4 (15)	C(26)-P(1)-C(36)	107.4 (15)
Au(2)-P(2)-C(46)	120.0 (9)	Au(2)-P(2)-C(56)	111.2 (12)
C(46)-P(2)-C(56)	104.8 (14)	Au(2)-P(2)-C(66)	109.1 (10)
C(46)-P(2)-C(66)	104.8 (13)	C(56)-P(2)-C(66)	106.0 (13)
Au(3)-P(3)-C(76)	107.7 (9)	Au(3)-P(3)-C(86)	112.5 (10)
C(76)-P(3)-C(86)	104.1 (12)	Au(3)-P(3)-C(96)	117.5 (9)
C(76)-P(3)-C(96)	105.7 (12)	C(86)-P(3)-C(96)	108.2 (13)
Au(4)-P(4)-C(106)	110.9 (9)	Au(4)-P(4)-C(116)	110.8 (10)
C(106)-P(4)-C(116)	107.0 (13)	Au(4)-P(4)-C(126)	113.7 (11)
C(106)-P(4)-C(126)	108.2 (13)	C(116)-P(4)-C(126)	106.0 (14)
Au(1)-S(1)-Au(2)	83.9 (4)	Au(1)-S(1)-C(1)	108.8 (14)
Au(2)-S(1)-C(1)	108.1 (14)	Au(3)-S(2)-Au(4)	82.1 (3)
Au(3)-S(2)-C(2)	105.5 (14)	Au(4)-S(2)-C(2)	105.8 (14)
S(1)-C(1)-C(206)	108.5 (26)	S(2)-C(2)-C(216)	130.3 (35)
S(2)-C(2)-C(226)	113.2 (34)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

bond distances and angles are listed in Table III. **1** consists of two cationic $Au_2(PPh_3)_2(\mu\text{-}SCH_2Ph)^+$ units. The two Au atoms in each unit are bridged by the $-SCH_2Ph$ ligand with an Au(1)-Au(2) separation of 3.142 (3) Å and an Au(3)-Au(4) separation of 3.077 (3) Å. These Au-Au separations are similar to that found in[3b] $[Au(PPh_3)]_2(\mu\text{-}i\text{-}MNT)$ and can be attributed to the bridging effects. Au(1) and Au(4) atoms have a linear coordination geometry, S(1)-Au(1)-P(1) = 174.8 (4)° and P(4)-Au(4)-S(2) = 175.8 (4)°, while Au(2) and Au(3) are off linearity by about 10°, S(1)-Au(2)-P(2) = 170.4 (4)° and S(2)-Au(3)-P(3) = 169.4 (4)°, presumably caused by steric effects.

A remarkable feature of compound **1** is the aggregation of the two monocations to form a tetranuclear rhombic cluster. The rhombus has a dihedral angle of 13.8° between the Au(1)Au(2)Au(3) plane and the Au(1)Au(4)Au(3) plane. The intercationic distances of Au(1)-Au(4) = 3.077 (2) Å and Au(2)-Au(3) = 3.194 (2) Å are similar to the intracationic Au-Au distances. A similar rhombic Au_4 arrangement was observed in $[Au(PhNNNPh)]_4$ where all Au atoms are bridged by PhNNNPh ligands.[5] It is apparent that Au^I-Au^I interactions are the driving force causing the aggregation of two cations in **1**. Similar dimerizations of two monocations resulting in short interionic Au^I-Au^I separations have also been observed in[6a,b] $[HgAu(CH_2PPh_2S)_2]_2[PF_6]_2$ (Au-Au = 3.150 (2) Å), $[Au(Py)_2]_2[AuI_2]_2$ (Au-Au = 3.291 (1) Å), and[6c] $\{[Au(PPh_3)]_3S\}_2(PF_6)_2$ (Au-Au = 3.236, 3.361 Å). Short intermolecular Au-Au separations without bridging ligands have been reported in several one-dimensional chain compounds such as[7a-c] $Au_2Pt(CH_2PPh_2S)_4$, $Au_2Pb(CH_2PPh_2S)_4$, $Au_2(CH_2PPh_2S)_2$, and $Au_2(S_2PR_2)_2$, where R = isopropyl,[7d] and $Au_2(S_2CNR_2)_2$, where R = *n*-propyl[7e] and *n*-butyl.[7f] Such weak Au-Au interactions have been attributed to the pronounced relativistic effects on the valence orbitals of gold atoms, which promote the mixing of the filled 5d orbitals with the empty 6s and 6p orbitals.[8] Theoretical calculations on binuclear and polynuclear gold complexes have suggested that such mixing may be responsible for the weak Au^I-Au^I interactions.[9] Further evidences for the presence of Au-Au interactions in **1** are from the fact that this cluster luminesces in the solid state. Previous studies on several luminescent dinuclear gold(I) com-

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)[a] for $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$ (**2**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au(1)	4890 (1)	1537 (1)	5524 (1)	55 (1)*
Au(2)	5499 (1)	-354 (1)	7901 (1)	40 (1)*
S(1)	3039 (8)	1526 (5)	7038 (4)	48 (2)*
S(2)	7478 (8)	361 (5)	6685 (4)	53 (2)*
Cl(1)	3374 (8)	-906 (6)	9065 (4)	58 (2)*
Cl(2)	8078 (8)	-2201 (5)	8614 (4)	62 (2)*
Cl(3)	6928 (13)	1433 (8)	4101 (5)	104 (4)*
Cl(4)	2189 (12)	2658 (7)	4496 (5)	94 (4)*
C(11)	2428 (19)	4365 (14)	6995 (8)	54 (9)*
C(12)	2309 (19)	5609 (14)	7452 (8)	77 (11)*
C(13)	2856 (19)	5542 (14)	8512 (8)	58 (10)*
C(14)	3522 (19)	4231 (14)	9115 (8)	62 (10)*
C(15)	3641 (19)	2988 (14)	8659 (8)	52 (8)*
C(16)	3094 (19)	3055 (14)	7598 (8)	49 (8)*
C(21)	7416 (19)	3113 (15)	6813 (8)	56 (10)*
C(22)	7787 (19)	4160 (15)	7335 (8)	77 (12)*
C(23)	8545 (19)	3846 (15)	8367 (8)	67 (11)*
C(24)	8931 (19)	2486 (15)	8877 (8)	63 (11)*
C(25)	8560 (19)	1439 (15)	8354 (8)	62 (10)*
C(26)	7803 (19)	1753 (15)	7322 (8)	47 (9)*

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

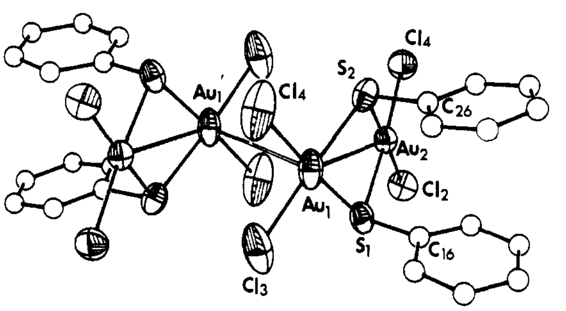

Figure 2. Dimeric structure of **2** showing 50% thermal ellipsoids and labeling scheme.

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Table V. Selected Bond Lengths (Å) and Angles (deg) for $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$ (**2**)[a]

	A. Bond Lengths		
Au(1)–Au(2)	3.357 (1)	Au(1)–S(1)	2.332 (5)
Au(1)–S(2)	2.339 (5)	Au(1)–Cl(3)	2.310 (8)
Au(1)–Cl(4)	2.295 (7)	Au(2)–S(1)	2.329 (5)
Au(2)–S(2)	2.338 (6)	Au(2)–Cl(1)	2.308 (6)
Au(2)–Cl(2)	2.289 (5)	S(1)–C(16)	1.758 (15)
S(2)–C(26)	1.761 (17)		
	B. Bond Angles		
Au(2)–Au(1)–S(1)	43.9 (1)	Au(2)–Au(1)–S(2)	44.1 (1)
S(1)–Au(1)–S(2)	84.1 (2)	Au(2)–Au(1)–Cl(3)	131.7 (2)
S(1)–Au(1)–Cl(3)	175.5 (2)	S(2)–Au(1)–Cl(3)	91.5 (2)
Au(2)–Au(1)–Cl(4)	131.1 (2)	S(1)–Au(1)–Cl(4)	91.2 (2)
S(2)–Au(1)–Cl(4)	175.2 (2)	Cl(3)–Au(1)–Cl(4)	93.2 (3)
Au(1)–Au(2)–S(1)	44.0 (1)	Au(1)–Au(2)–S(2)	44.1 (1)
S(1)–Au(2)–S(2)	84.2 (2)	Au(1)–Au(2)–Cl(1)	132.4 (1)
S(1)–Au(2)–Cl(1)	91.7 (2)	S(2)–Au(2)–Cl(1)	175.8 (2)
Au(1)–Au(2)–Cl(2)	130.9 (1)	S(1)–Au(2)–Cl(2)	174.9 (2)
S(2)–Au(2)–Cl(2)	91.0 (2)	Cl(1)–Au(2)–Cl(2)	93.1 (2)
Au(1)–S(1)–Au(2)	92.1 (2)	Au(1)–S(1)–C(16)	100.9 (5)
Au(2)–S(1)–C(16)	104.9 (4)	Au(1)–S(2)–Au(2)	91.7 (2)
Au(1)–S(2)–C(26)	103.5 (4)	Au(2)–S(2)–C(26)	101.0 (5)
S(1)–C(16)–C(11)	119.0 (4)	S(1)–C(16)–C(15)	120.8 (4)
S(2)–C(26)–C(21)	122.3 (4)	S(2)–C(26)–C(26)	117.7 (4)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

plexes suggested that luminescence of these complexes may be caused by Au–Au interactions.[10]

Synthesis and Crystal Structure of $Au^{III}_2Cl_4(\mu\text{-}SPh)_2$ (2). The reaction of $Au^I(CO)Cl$ with excess PhSSPh in CH_2Cl_2 yielded the red-orange compound **2** as a major product. Compound **2** is apparently the result of oxidative addition of PhSSPh to the Au^I center. **2** was characterized by elemental and single-crystal X-ray diffraction analysis.

Atomic positional and thermal parameters are given in Table IV. Bond lengths and angles are given in Table V. The molecular structure of **2** is shown in Figure 2. Au atoms are coordinated by two chlorine atoms and bridged by two –SPh ligands. Each Au atom has a square-planar geometry. The S(1) and S(2) separation is 3.129 Å. The two phenyl rings are nearly parallel to each other with a dihedral angle of 11.8°. The longest distance between the two phenyl rings is C(23)–C(13) = 3.98 Å, and the shortest separation is C(26)–C(16) = 3.31 Å, similar to the nonbonding separation in graphite.[11] The structure of **2** is similar to that of a known compound $Au_2(CH_3)_4(\mu\text{-}SC_2H_5)_2$ reported previously.[12] However, the Au–S distance (2.33 Å in average) in **2** is much shorter than that in $Au_2(CH_3)_4(\mu\text{-}SC_2H_5)_2$ (2.42 Å in average), obviously due to the relatively strong trans effect of CH_3 groups. The dihedral angle of the Au_2S_2 rhombus defined by the S(1)Au(1)S(2) and S(1)Au(2)S(2) planes, 150.3°, is much larger than that in $Au_2(CH_3)_4(\mu\text{-}SC_2H_5)_2$, 141.3°. The Au(1)–Au(2) separation of 3.357 (1) Å is, however, significantly shorter than that in $Au_2(CH_3)_4(\mu\text{-}SC_2H_5)_2$, 3.457 (3) Å. Therefore, the short Au–S bonds in **2** could be the dominating force in bringing the two Au atoms closer than in $Au_2(CH_3)_4(\mu\text{-}SC_2H_5)_2$. An important feature of this molecule is that it dimerizes in the solid state, as shown in Figure 2. The S(1)S(2)Au(1)Cl(3)Cl(4) unit is parallel to the same unit in the neighboring molecule with chlorine atoms eclipsed with sulfur atoms and an Au(1)–Au(1′) separation of 3.416 (1) Å (Figure 3). Although it is very common for square-planar Pt^{II} complexes to form staggered or eclipsed one-dimensional chain structures with weak Pt–Pt interactions in the solid state,[13] it is rare for the isoelectronic square-planar Au^{III} complexes to form staggered or eclipsed structures in the solid state. Instead, Au^{III} complexes tend to form five-coordinated species in the solid state with a long axial Au–L bond.[14] To our knowledge, **2** is the first example with such a short intermolecular Au^{III}–Au^{III} separation and eclipsed geometry.

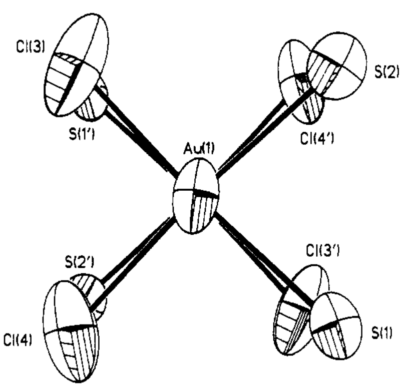

Figure 3. Diagram showing the eclipsed structure of the Au(1) and Au(1′) units.

Oxidation products of reductions of organic disulfides by monomeric gold(I) complexes have not been characterized previously, although reactions have been described.[1e] The formation of **1** and **2** demonstrates that monomeric gold(I) complexes, as well as dimeric species, can reduce disulfides, although the reaction mechanism remains to be established.

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Supplementary Material Available: Tables of crystallographic data, H atom parameters, and anisotropic temperature factors for **1** and **2** and a full listing of atomic positional parameters for **1** (12 pages); Tables listing observed and calculated structure factors for **1** and **2** (79 pages). Ordering information is given on any current masthead page.

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