Synthesis and Structural Characterization of Tetranuclear Sulfur-Centered Complexes with Mixed-Valent Gold Atoms: $[S(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ (dppf = 1,1′-Bis(diphenylphosphino)ferrocene) and $[S(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$

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The reaction of $[S(Au_2dppf)]$ or $[S(AuPPh_3)_2]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 2 equivs of $[Au(C_6F_5)_3(OEt_2)]$ leads to the tetranuclear gold(I)−gold(III) derivatives $[S(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ (**1**) or $[S(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$ (**2**), which contain a μ_4-sulfur moiety. The crystal structure determinations reveal a tetrahedral coordination at the sulfur center, more distorted in complex **1** as a consequence of a short gold(I)−gold(I) interaction of 2.9561(7) Å and a gold(I)−gold(III) contact of 3.534 Å.

Introduction

The aggregation of (phosphine)gold(I) fragments at small interstitial atoms has attracted much attention in the last few years,[1−3] not only from the experimental but also from the theoretical standpoint. The unusual structure and bonding of both the central heteroatom and the gold atoms have been the subject of many theoretical studies.[4−9] One particular feature of these complexes is that they are stabilized by energetically favorable interactions between the formally closed-shell (d^{10}) gold atoms. This type of interaction, termed "aurophilicity", operates at distances of ca. 3.0 Å and is associated with bond energies of ca. 33 kJ/mol;[10−13] it has been shown to arise from relativistic and correlation effects.[6,7,14,15]

In our studies of sulfur-centered phosphine−gold complexes we have previously reported the synthesis and structural characterization of the tetraaurated species $[S(AuPPh_3)_4]^{2+}$ [16,17] or $[S(Au_2dppf)_2(AuPPh_2Me)_2]^{2+}$.[18] These studies have revealed that both complexes were electron deficient, with a square pyramidal or a distorted trigonal bipyramidal geometry, and that not only electronic but also steric effects of the ligand are important for the final structural framework.

However, no studies have been directed at the coordination of gold fragments in different oxidation states in such central heteroatom complexes. Thus it would be interesting to know if gold(III) centers are capable of taking part in this type of gold−gold interactions. Here we report the first examples of the synthesis, characterization, and crystal structures of the novel μ_4-sulfido tetranuclear mixed gold(I)−gold(III) derivatives, which show a tetrahedral geometry at the sulfur center, in contrast to that previously described for the gold(I) complexes.

Results and Discussion

The reaction of the dinuclear complexes $[S(Au_2dppf)]$ or $[S(AuPPh_3)_2]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 2 equivs of $[Au(C_6F_5)_3(OEt_2)]$ in dichloromethane affords the tetranuclear mixed species $[S(Au_2dppf)\{Au(C_6F_5)_3\}_2]$ (**1**) or $[S(AuPPh_3)_2\{Au(C_6F_5)_3\}_2]$ (**2**), respectively, in high yield. These complexes are orange

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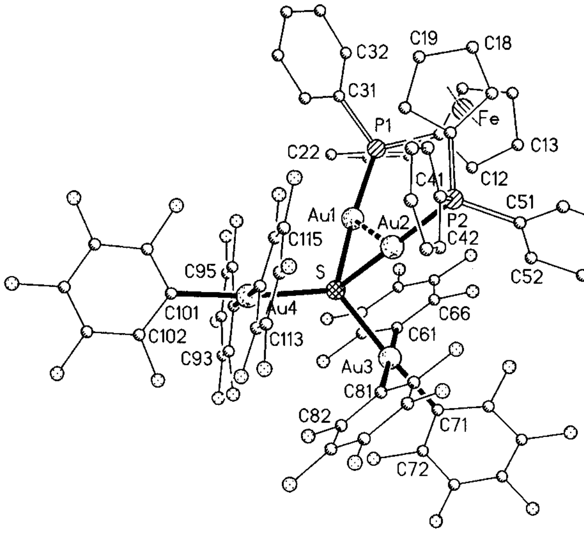

Figure 1. Structure of complex **1** in the crystal showing the atom-numbering scheme. Radii are arbitrary. The H atoms are omitted for clarity.

(**1**) or white (**2**) solids, stable to air and moisture. Their conductivity in acetone solutions is about 21 Ω^{-1} cm^2 mol^{-1}; this value is rather high for a neutral complex, but we postulate that a partial dissociation of one $AuPPh_3^+$ fragment, giving $[Au(PPh_3)(Me_2CO)]^+$ and $[S(AuPPh_3)\{Au(C_6F_5)_3\}_2]^-$, can take place in a donor solvent such as acetone. In the IR spectra the absorptions arising from pentafluorophenyl groups bonded to gold(III) appear at *ca.* 1507 (s) and 967 (s) cm^{-1}; however the vibrations ν(Au−S), which usually appear around or below 300 cm^{-1}, are too weak to be observed.

The $^{31}P\{^1H\}$ NMR spectra show one singlet for the two equivalent phosphorus atoms at δ 28.5 (**1**) and 34.5 (**2**). We have observed an upfield displacement when a new gold fragment coordinates to the sulfur center,[17,18] although the shift observed for the coordination of two gold(III) fragments is smaller ($\Delta \approx 1.6$ ppm) than those for the coordination of two gold(I) units ($\Delta \approx 3.7$ ppm). In the ^{1}H NMR spectrum for complex **1** two broad bands are present for the cyclopentadienyl protons. When the experiment was carried out at −55 °C, four multiplets associated with the inequivalent α and β protons of the two cyclopentadienyl rings appear at 4.57, 4.48, 4.16, and 3.38 ppm. The high-field displacement of one of the signals is noteworthy; we have usually observed the resonances of the α and β protons of the dppf ligand above 4 ppm. The reason could be that these protons are situated closer to the gold atoms, whose electron density provides better shielding.

The positive fast atom bombardment spectra for complexes **1** and **2** do not show the molecular peaks; instead other fragments arising from the loss of pentafluorophenyl groups or gold atoms appear: **1**, m/z = 1511 ($[M - 5C_6F_5]^+$, 8%), 1409 ($[S(AuPPh_3)_3]^+$, 17%), 1117 ($[M - 5C_6F_5 - 2Au]^+$, 14%); **2**, m/z = 1147 ($[M - 4C_6F_5 - 2Au]^+$, 72%).

The structure of complex **1** (Figure 1) has been confirmed by X-ray diffraction studies. The geometry at the sulfur center is distorted tetrahedral, the main distortion involving the extremely acute Au(1)−S−Au(2) angle of 78.30(9)°. (N.B. In both complexes Au(1) and Au(2) are gold(I) and Au(3) and Au(4) are gold(III)). The Au(3)−S−Au(4) angle of 126.22(13)° is the widest. However, there is a difference in the angles between the gold(I) and the gold(III) centers, Au(1)−S−Au(4) = 111.94(12)° and Au(2)−S−Au(3) = 96.84(11)°. Of necessity, narrower Au−S−Au angles are correlated with shorter gold−gold contacts; there is an obvious gold(I)−gold(I) interaction of 2.9561(7) Å (which corresponds to the narrowest angle) but two different gold(I)−gold(III) contacts of 3.533(1) Å [Au(2)−Au(3)] and 3.915(1) Å [Au(1)−Au(4)]. The gold(I)−gold(I) interaction in complex **1** is of the same order as others found in this type of sulfur-centered derivatives;[16−21] we have little data concerning gold(I)−gold(III) contacts, but the shortest found in complex **1** is only slightly longer that the longest gold(I)−gold(I) interactions in many complexes or gold−gold bonds in gold clusters.[22,23] As far as we are aware, this is one of the shortest reported gold(I)−gold(III) interactions to date, not taking into account the gold−gold contacts in the mixed-valent Au(I)-Au(III) doubled-bridged ylide systems,[24−27] where the gold atoms are forced to be in close proximity. The distance between the two gold(III) centers, 4.250 Å, is too long to be considered as an interaction.

The Au−S bond lengths are 2.339(3) and 2.343(3) Å to the two gold(I) units and 2.385(3) and 2.380(3) Å to the two gold(III) centers; these are shorter than those found in $[S(AuPPh_3)_4]^{2+}$ [2.362(5)−2.429(5) Å][16] and are similar to those in $[S(Au_2dppf)(AuPPh_2Me)_2]^{2+}$ [2.309(5)−2.416(5) Å].[18] Surprisingly, the Au(III)−S distances are longer than Au(I)−S in contrast to most literature observations.

The structure of compound **2** (Figure 2) has also been determined by X-ray diffraction. The geometry around the sulfur center is tetrahedral and less distorted than in complex **1**. This can be seen in the Au(1)−S−Au(2) angle of 87.75(11)°, much wider than in **1**. Correspondingly the gold(I)−gold(I) interaction is longer than in complex **1**, 3.2244(10) Å. Furthermore, as the other angles are closer to the ideal values for a tetrahedron, the gold(I)−gold(III) distances are longer than in **1**, 3.740(1)−4.011(1) Å. The Au-S bond lengths are 2.319(3) and 2.333(3) Å to gold(I) and 2.385(3) and 2.387(3) Å to gold(III), similar to those in compound **1** and showing the same pattern of shorter distances to gold(I). The dihedral angle between the two AuSAu planes is 97.5°.

Experimental Section

Instrumentation and Materials. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 2000−200 cm^{-1}, using Nujol mulls between polyethylene sheets. ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian UNITY 300 spectrometer in $CDCl_3$ solutions; chemical shifts are quoted relative to $SiMe_4$ (^{1}H, external), $CFCl_3$ (^{19}F,

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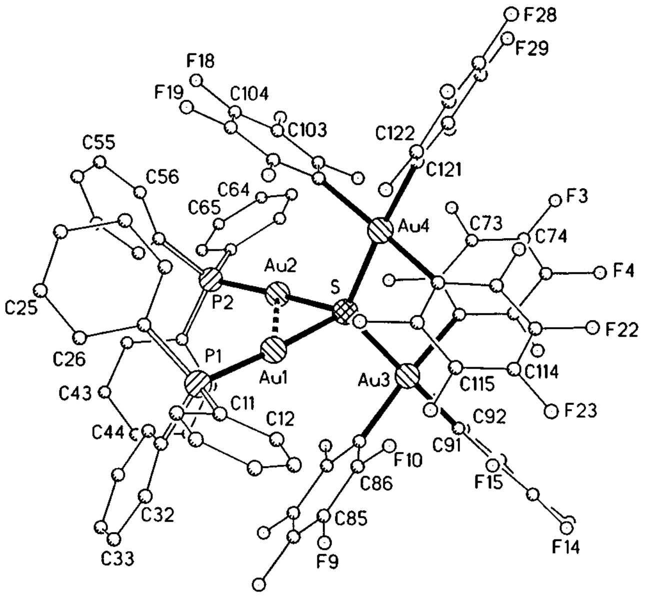

Figure 2. Perspective view of complex **2** in the crystal with the atom-labeling scheme. Radii are arbitrary. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 1

Au(1)−P(1)	2.254(3)	Au(1)−S	2.339(3)
Au(1)−Au(2)	2.9561(7)	Au(2)−P(2)	2.252(3)
Au(2)−S	2.343(3)	Au(3)−C(71)	1.979(13)
Au(3)−C(61)	2.067(10)	Au(3)−C(81)	2.093(10)
Au(3)−S	2.380(3)	Au(4)−C(101)	2.034(12)
Au(4)−C(111)	2.057(11)	Au(4)−C(91)	2.069(11)
Au(4)−S	2.385(3)	Au(1)···Au(3)	3.947(1)
Au(2)···Au(3)	3.533(1)	Au(1)···Au(4)	3.915(1)
Au(2)···Au(4)	4.081(1)	Au(3)···Au(4)	4.250(1)
P(1)−Au(1)−S	170.39(11)	P(1)−Au(1)−Au(2)	119.48(8)
S−Au(1)−Au(2)	50.91(7)	P(2)−Au(2)−S	173.90(10)
P(2)−Au(2)−Au(1)	123.66(8)	S−Au(2)−Au(1)	50.79(7)
C(71)−Au(3)−C(61)	87.5(4)	C(71)−Au(3)−C(81)	92.3(4)
C(61)−Au(3)−C(81)	178.8(3)	C(71)−Au(3)−S	175.8(3)
C(61)−Au(3)−S	89.6(3)	C(81)−Au(3)−S	90.6(3)
C(101)−Au(4)−C(111)	87.5(4)	C(101)−Au(4)−C(91)	90.4(4)
C(111)−Au(4)−C(91)	177.9(4)	C(101)−Au(4)−S	174.0(3)
C(111)−Au(4)−S	92.1(3)	C(91)−Au(4)−S	90.0(3)
Au(1)−S−Au(2)	78.30(9)	Au(1)−S−Au(3)	113.48(11)
Au(2)−S−Au(3)	96.84(11)	Au(1)−S−Au(4)	111.94(12)
Au(2)−S−Au(4)	119.35(12)	Au(3)−S−Au(4)	126.22(13)

external), and H_3PO_4 (^{31}P, external). C, H, and S analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} acetone solutions with a Philips 9509 conductimeter, and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. Mass spectra were recorded on a VG Autospec using FAB techniques and nitrobenzyl alcohol as matrix. The starting materials [S(Au$_2$dppf)],[18] [S(AuPPh$_3$)$_2$],[17] and [Au(C_6F_5)$_3$(OEt$_2$)][28] were prepared as described earlier.

Syntheses. [S(Au$_2$dppf){Au(C_6F_5)$_3$}$_2$] (1). To a solution of [S(Au$_2$dppf)] (0.059, 0.06 mmol) in dichloromethane (20 mL) was added [Au(C_6F_5)$_3$(OEt$_2$)] (0.093 g, 0.12 mmol), and the mixture was stirred for 5 min. The solvent was evaporated to ca. 5 mL, and addition of *n*-hexane (15 mL) gave a yellow solid of **1** which was separated by filtration. Yield: 77%. Anal. Calcd for $C_{70}H_{28}Au_4F_{30}FeP_2S$: C, 35.25; H, 1.12; S, 1.56. Found: C, 35.38; H, 1.12; S, 1.35. ^{19}F (−55 °C): −121.0 (m, br, 4F, *o*-F), −122.2 (m, 8F, *o*-F), −155.8 (m, br, 4F, *p*-F), −156.5 [t, 2F, *p*-F, ^3J(FF) 20.4 Hz], −160.8 (m, 8F, *m*-F), −161.7 (m, 4F, *m*-F).

[S(AuPPh$_3$)$_2${Au(C_6F_5)$_3$}$_2$] (2). To a suspension of [S(AuPPh$_3$)$_2$] (0.057 g, 0.06 mmol) in diethyl ether (20 mL) was added [Au(C_6F_5)$_3$(OEt$_2$)] (0.093 g, 0.12 mmol), and the mixture was stirred until the starting material had dissolved. The solvent was evaporated to dryness and the residue dissolved in 5 mL of dichloromethane; addition of *n*-hexane led to an oil that upon cooling to −20 °C gave a white solid of complex **2**. Yield: 75%. Anal. Calcd for $C_{72}H_{30}Au_4F_{30}P_2S$: C, 36.85; H, 1.29; S, 1.37. Found: C, 37.10; H, 1.29; S, 1.47. ^{19}F: −120.5 (m, 8F, *o*-F), −122.2 (m, 4F, *o*-F), −161.2 (m, 8F, *m*-F), −161.7 (m, 4F, *m*-F), −156.7 [t, 4F, *p*-F, ^3J(FF) 20.0 Hz], −157.3 [t, 2F, *p*-F, ^3J(FF) 20.0 Hz].

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Au(1)−P(1)	2.263(4)	Au(1)−S	2.333(3)
Au(1)−Au(2)	3.2244(10)	Au(2)−P(2)	2.253(4)
Au(2)−S	2.319(3)	Au(3)−C(91)	2.01(2)
Au(3)−C(91¢)	2.04(2)	Au(3)−C(81)	2.051(12)
Au(3)−C(71)	2.09(2)	Au(3)−S	2.385(3)
Au(4)−C(101)	2.018(13)	Au(4)−C(111)	2.064(13)
Au(4)−C(121)	2.091(13)	Au(4)−S	2.387(3)
Au(1)···Au(3)	4.011(1)	Au(1)···Au(4)	3.740(1)
Au(2)···Au(3)	3.809(1)	Au(2)···Au(4)	3.985(1)
Au(3)···Au(4)	4.128(1)		
P(1)−Au(1)−S	176.66(13)	P(1)−Au(1)−Au(2)	132.80(11)
S−Au(1)−Au(2)	45.94(8)	P(2)−Au(2)−S	175.14(13)
P(2)−Au(2)−Au(1)	128.87(10)	S−Au(2)−Au(1)	46.31(8)
C(91)−Au(3)−C(81)	88.0(9)	C(91¢)−Au(3)−C(81)	88.3(9)
C(91)−Au(3)−C(71)	86.7(9)	C(91¢)−Au(3)−C(71)	86.8(9)
C(81)−Au(3)−C(71)	174.4(5)	C(91)−Au(3)−S	174.6(5)
C(91¢)−Au(3)−S	175.1(4)	C(81)−Au(3)−S	91.1(3)
C(71)−Au(3)−S	94.0(3)	C(101)−Au(4)−C(111)	88.1(4)
C(101)−Au(4)−C(121)	89.7(5)	C(111)−Au(4)−C(121)	172.3(4)
C(101)−Au(4)−S	176.3(3)	C(111)−Au(4)−S	88.9(3)
C(121)−Au(4)−S	93.4(3)	Au(2)−S−Au(1)	87.75(11)
Au(2)−S−Au(3)	108.14(13)	Au(1)−S−Au(3)	116.46(13)
Au(2)−S−Au(4)	115.70(13)	Au(1)−S−Au(4)	104.78(13)
Au(3)−S−Au(4)	119.76(13)		

Table 3. Details of Data Collection and Structure Refinement for Complexes 1 and 2

	compd	
	1·CH_2Cl_2	2·CH_2Cl_2
chem formula	$C_{71}H_{30}Au_4Cl_2F_{30}FeP_2S$	$C_{73}H_{32}Au_4Cl_2F_{30}P_2S$
cryst habit	orange tablet	colorless prism
cryst size/mm	0.40 × 0.20 × 0.08	0.38 × 0.19 × 0.15
space group	$P\bar{1}$	$P2_1/n$
a/Å	13.021(2)	13.138(4)
b/Å	13.829(2)	21.118(6)
c/Å	20.145(2)	26.530(7)
α/deg	86.707(8)	
β/deg	79.431(8)	92.37(3)
γ/deg	78.421(10)	
V/Å^3	3492.5(7)	7354(4)
Z	2	4
D_c/Mg m^{-3}	2.341	2.196
M	2461.57	2431.75
F(000)	2296	4544
T/°C	−100	−100
$2\theta_{max}$/deg	50	45
μ(Mo Kα)/mm^{-1}	8.85	8.219
transm	0.643−1.0	0.355−0.755
no. of reflcns measd	13795	10101
no. of unique reflcns	12197	9582
R_{int}	0.076	0.063
R^a (F, $F > 4s(F)$)	0.045	0.044
wR^b (F^2, all reflcns)	0.096	0.112
no. of params	667	993
no. of restraints	444	1042
S^c	0.865	1.075
max Δρ/e Å^{-3}	1.6	1.79

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] w$R(F^2) = [\sum\{w(F_o^2 - F_c^2)2\}/\sum\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [c] $S = [\sum\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibers. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). Diffractometer

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type: Siemens P4 (**1**) and Stoe AED-2 (**2**) equipped with a Siemens or Oxford low temperature attachment. The scan type was ω (**1**) or ω/θ (**2**). Cell constants were refined from setting (**1**) or $\pm\omega$ (**2**) angles of *ca.* 50 reflections in the range 2θ 20−23°. Absorption corrections were applied on the basis of ψ-scans. Structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-93)[29] for all atoms (exceptions: isotropic phenyl rings and solvent atoms in **1**; disordered atoms and solvent carbon atom of **2**). One C_6F_5 ring of **2** (C(91−96), F(11−15)) is disordered over two positions. Both complexes crystallize with one molecule of dichloromethane, poorly resolved because of disorder or high displacement parameters. Selected bond lengths and angles for **1** and **2** are given in Tables 1 and 2. Crystal data are collected in Table 3.

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Supporting Information Available: Tables of crystal data, data collection, and solution and refinement parameters, positional and thermal parameters, bond distances and angles, and anisotropic thermal parameters and ORTEP diagrams (22 pages). Ordering information is given on any current masthead page.

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