Auriophilicity in Polynuclear (Phosphane)gold(I) Thiolates $\{Me_3CS[Au(PPh_3)]_2\}^+ BF_4^-$ and $\{(CH_2S)_2[Au(PPh_3)]_3\}^+ BF_4^-$

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Received May 12, 1995

Key Words: Gold(I) thiolates / (1,2-Ethanedithiolato)gold(I) complexes / (*tert*-Butanethiolato)gold(I) complexes / Polynuclear gold(I) complexes

The reaction of *tert*-butanethiol with tris[(triphenylphosphane)gold(I)]oxonium tetrafluoroborate in dichloromethane in the presence of sodium tetrafluoroborate gave quantitative yields of a product $\{Me_3CS[Au(PPh_3)]_2\}^+ BF_4^-$ (**1**). In the crystal lattice of this salt, the sulfonium cations are associated into dimers through close Au···Au contacts. The centrosymmetrical tetranuclear unit has Au···Au distances of 3.292(1) and 3.206(1) Å, and the Au−S−Au angles are exactly 90.0(1)°. Both data are indicative of significant intra- and intercationic Au···Au attractions. The analogous reaction of ethane-1,2-dithiol afforded high yields of a product $\{(CH_2S)_2[Au(PPh_3)]_3\}^+ BF_4^-$ (**2**). The compound is fluxional in CD_2Cl_2 solution and shows only one ^{31}P-NMR signal at −60 °C. In the crystal, the quasi C_2-symmetrical trinuclear cations feature the sulfur atoms in bridging positions between two gold atoms. The central gold atom is thus three-coordinate; the peripheral gold atoms are two-coordinate with Au···Au contacts at 3.284(1) and 3.129(1) Å and Au−S−Au angles as small as 86.5(1) and 81.0(1)°. This provides clear evidence for "auriophilic" bonding.

Gold(I) thiolates are the most widely used compounds of gold in medicine and in surface technology[1,2]. Virtually all of the classical and modern gold drugs for arthritis and rhematism have been based on various gold-sulfur compounds[3−5]. The pastes addressed as "liquid gold" in use for gold plating of glass and ceramics are mixtures of gold(I) thiolates derived from natural products; furthermore, precursors of advanced gold thin film technology are still relying mainly on the special properties of gold-sulfur systems[6].

Surprisingly, only few of these materials have been properly identified, and it is only recently that major progress has been made regarding the full characterization of specific gold(I) thiolates[7]. As part of our own studies, we now report on the synthesis and structural characterization of cationic polynuclear gold(I) complexes of an aliphatic monothiol (*tert*-butanethiol, Me_3CSH) and the most simple alkane dithiol, dithioglycol (1,2-ethanedithiol, $HSCH_2CH_2SH$). Previous structural studies focussed mainly on compounds of benzenethiols, including thiophenol, benzenedithiols, toluenedithiols, and benzenehexathiol, but included also a benzylthiolate[8−12].

The reaction of *tert*-butanethiol (Me_3CSH) with tris[(triphenylphospane)gold(I)]oxonium tetrafluoroborate in dichloromethane in the presence of sodium tetrafluoroborate, afforded high yields of a sulfonium salt with a dinuclear cation according to the following equation:

$$Me_3CSH + [(Ph_3P)Au]_3O^+BF_4^- \rightarrow \underset{\mathbf{1}}{Me_3CS[Au(PPh_3)]_2^+BF_4^-} + H_2O$$

The product (**1**) was obtained as colorless crystals, stable in air and moisture, and readily soluble in polar organic solvents without decomposition. The dry solid decomposes at 164 °C. The mass spectrum (FAB) shows the cation of the salt as the parent peak [*m/z* = 1007.1 (100%)]. The ^{31}P-NMR spectrum has a single line at $\delta = 35.9$ (in $CDCl_3$), and the ^{13}C-NMR spectrum has one set of phenyl carbon atoms and two resonances for the *t*-butyl group.

Compound **1** crystallizes from diethyl ether/dichloromethane in the triclinic space group $P\bar{1}$ (No. 2) with two molecular units in the unit cell. The BF_4^- anions and the sulfonium cations have no sub-van-der-Waals contacts. In the crystal, the cations are tetranuclear dimers with a crystallographic center of inversion in the middle of a parallelogram of gold atoms (Figure 1).

While the neighboring Au−Au distances are very similar, the Au−Au−Au angles are quite different [3.206(1) and 3.292(1) Å, 81.4(1) and 98.6(1)°]. The two shorter edges [Au1−Au2] are bridged by the thiolate ligands above and below the molecular plane. The gold and sulfur atoms thus form a six-membered ring in a "steep" chair form. The sulfur atoms have a pyramidal configuration with small angles Au−S−Au [90.0(1)°]. This structure thus resembles quite closely the structure reported for the corresponding benzylthiolate (with nitrate counterions)[12]. It is particularly noteworthy that in both cases the intra- and intermolecular Au···Au distances within or between the monomeric units differ very little, indicating quite significant auriophilic bonding between these units.

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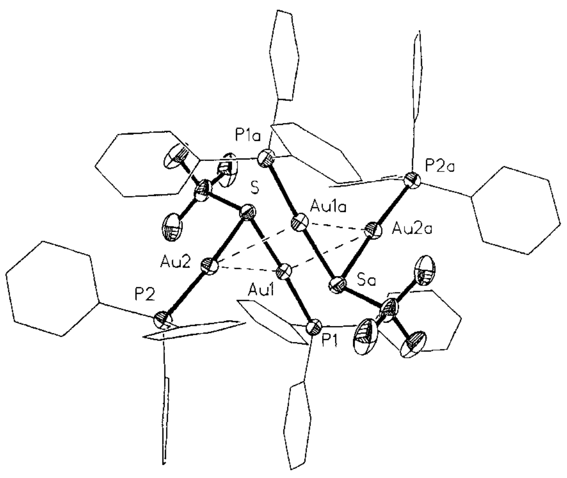

Figure 1. Structure of a cation-dimer in the crystal of $\{Me_3CS[Au(PPh_3)]_2\}^+$ BF_4^- (**1**) with atomic labeling. The unit has a center of inversion. (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity.) Selected bond lengths [Å] and angles [°]: Au1−Au2 3.292(1), Au1−Au2a 3.206(1), Au1−S 2.325(1), Au2−S 2.329(1), Au1−P1 2.274(1), Au2−P2 2.273(1), S−C 1.881(5). Au1−S−Au2 90.0(1), Au1−Au2−Au1a 81.4(1), Au2−Au1−Au2a 98.6(1), S−Au1−P1 175.7(1), S−Au2−P2 173.7(1), Au1−S−C 109.3(1), Au2−S−C 104.7(2)

The analogous reaction of the oxonium salt with ethane-1,2-dithiol gave virtually quantitative yields of a sulfonium salt with a trinuclear cation:

$$(CH_2SH)_2 + [(Ph_3P)Au]_3O^+\ BF_4^- \rightarrow H_2O + (CH_2S)_2[Au(PPh_3)]_3^+\ BF_4^-$$

2

The general properties of the product (**2**, dec. temp. 169 °C) are similar to those of compound **1**, and the analytical and spectroscopic data are in full agreement with the proposed stoichiometry (see Experimental). Surprisingly however, the ^{31}P-NMR spectrum shows only a single resonance for all three phosphane ligands even at temperatures as low as −60 °C (in CD_2Cl_2). Accordingly the ^{13}C- and ^{1}H-NMR spectra exhibit only one set of phenyl resonances and singlets for the ethane moiety. These results suggest either a symmetrical structure with equivalent phosphane groups, which is unlikely, or a fluxional systems with very low activation energies for rearrangements.

Compound **2** crystallizes from diethyl ether/dichloromethane with one mole of dichloromethane in triclinic crystals, space group $P\bar{1}$ (No. 2), with two stoichiometric units in the unit cell. There are no unusually close contacts between cations and ions. The cations have no crystallographically imposed symmetry, but the structure of the molecular skeleton (without the phenyl groups) approaches the symmetry requirements of the chiral point group C_2 closely, with the twofold axis passing through the atoms P3 and Au3, and with the midpoint between C1 and C2 (Figure 2). The central gold atom (Au3) is three-coordinate, while the other two (Au1, Au2) are two-coordinate. The two sulfur atoms are pyramidal sulfonium centers with small angles Au1−S1−Au3 and Au2−S2−Au3 of 86.5(1) and 81.0(1)°, respectively. The corresponding Au1−Au3 and Au2−Au3 contacts are 3.284(1) and 3.129(1) Å long. As expected, the coordination number three, at the central gold atom Au3, is associated with longer Au−S distances compared to the peripheral two-coordinate gold atoms Au1 and Au2 (Figure 2).

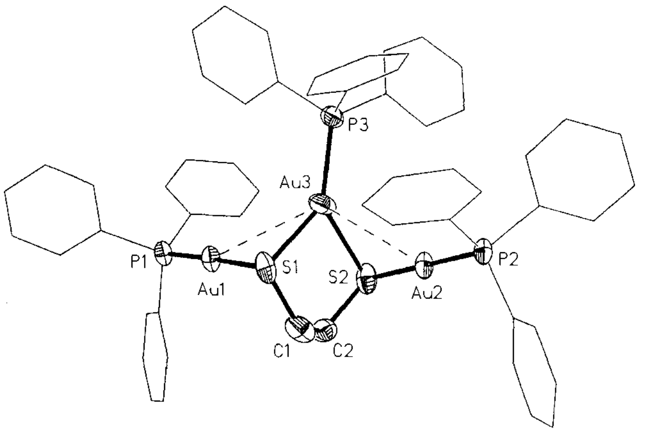

Figure 2. Structure of the cation in the crystal of $\{1,2\text{-}C_2H_4S_2[Au(PPh_3)]_3\}^+$ BF_4^- (**2**) with atomic labeling. (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity.) Selected bond lengths [Å] and angles [°]: Au1−Au3 3.284(1), Au2−Au3 3.129(1), Au1−S1 2.318(2), Au3−S1 2.472(3), Au3−S2 2.487(3), Au2−S2 2.326(2), Au1−P1 2.264(2), Au2−P2 2.273(2), Au3−P3 2.245(3). Au1−S1−Au3 86.5(1), Au2−S2−Au3 81.0(1), S1−Au1−P1 177.1(1), S2−Au2−P2 178.5(1), S1−Au3−P3 135.1(1), S2−Au3−P3 136.7(1), S1−Au3−S2 87.8(1)

To account for the NMR results (above) we propose a low activation energy process for the site exchange of the three Ph_3PAu groups between the two sulfur centers. Mechanistically, the most simple model would involve a cleavage of either bond Au3−S1 or bond Au3−S2, leading to independent $R-SAuPPh_3$ and $R-S(AuPPh_3)_2$ units, which can freely rotate about any of the remaining bonds (S−C, C−C) or undergo pyramidal inversion at the three-coordinate sulfur. Statistical recombination of a sulfur atom at Au3 or any other gold atom would equilibrate the Ph_3PAu units on the NMR time scale.

The structure of compound **2** thus closely resembles that of the trinuclear cation with a dithiocatecholate ligand 1,2-$C_6H_4S_2^{2-}$, that is, where a benzene ring is fused to C1 and C2 (for the atomic numbering, see Figure 2). This cation, $[1,2\text{-}C_6H_4S_2(AuPPh_3)_3]^+$, was investigated as the perchlorate salt, in which there are some long intermolecular contacts, which are absent in the lattice of compound **2**[10]. Parts of the structure are also related to coordination features of the phosphane-deficient species $[(1,2\text{-}C_6H_4)S_2Au_2(PR_3)]_2$ with three- and two-coordinate gold atoms[13,14]. All these structures are examples of molecules the configuration of which is strongly influenced by metal-metal interactions between low-coordinate gold atoms ("aurophilicity") and which exhibit the clear tendency for building cluster units within a given structural framework.

This work was supported by *Deutsche Forschungsgemeinschaft*, by *Fonds der Chemischen Industrie* and – through the donation of chemicals – by *Degussa AG* and *Heraeus GmbH*. Mr. *J. Riede* is thanked for carefully establishing the X-ray data sets.

Experimental

General: All experiments were carried out under dry, purified nitrogen. Samples and solutions were protected against direct incandescent light. Solvents were dried, distilled and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. *tert*-Butanethiol and ethane-1,2-dithiol were obtained commercially from Aldrich. MS: Varian MAT 311A; NMR: Jeol GX 400 spectrometer, $CDCl_3$, with TMS as an internal standard.

t-Butyl-bis[(triphenylphosphine)gold(I)]sulfonium Tetrafluoroborate (**1**): Tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (0.44 g, 0.30 mmol) is dissolved in 10 ml of dichloromethane. In the presence of 0.10 g of sodium tetrafluoroborate (0.91 mmol), 0.050 ml of *tert*-butanethiol (0.44 mmol) is added very slowly with stirring. After 1 h at room temperature the clear, orange solution is concentrated under vacuum and pentane is added. The orange precipitate is crystallized from CH_2Cl_2/Et_2O at room temperature. Colorless crystals, yield 0.48 g (100%), dec. temp. 164 °C. – ^1H NMR: δ = 1.62 (s, CH_3), 7.33–7.39 (m, Ph-*ortho*/*meta*), 7.53 (m, Ph-*para*). – $^{13}C\{^1H\}$ NMR: δ = 38.92 (s, CH_3), δ = 54.27 (s, *C*), 127.46 (d, $^1J_{CP}$ = 59.75 Hz, Ph-*ipso*), 129.56 (d, $^3J_{CP}$ = 11.95 Hz, Ph-*meta*), 132.49 (s, Ph-*para*), 133.62 (d, $^2J_{CP}$ = 13.78 Hz, Ph-*ortho*). – $^{31}P\{^1H\}$ NMR: δ = 35.92 (s, PPh_3). – MS (FAB): *m*/*z* (%) = 1007.1 (100) $[M^+]$. – $C_{40}H_{39}Au_2BF_4P_2S$ (1094.51): calcd. C 43.90, H 3.59, Au 35.99; found C 42.68, H 3.65, Au 35.84.

Table 1. Crystallographic data for **1** and **2**

	1	**2**
empirical formula	$C_{40}H_{39}Au_2BF_4P_2S$	$C_{56}H_{49}Au_3BF_4P_3S_2$ $*2CH_2Cl_2$
formula weight	1094.45	1726.54
crystal system	triclinic	triclinic
space group (No.)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)
a [Å]	10.989 (1)	14.102 (2)
b [Å]	12.933 (1)	14.609 (2)
c [Å]	14.776 (1)	17.693 (3)
α [°]	81.60 (1)	101.56 (1)
β [°]	68.76 (1)	113.09 (1)
γ [°]	81.44 (1)	92.80 (1)
V [$Å^3$]	1925.8	3252.0
ρ_{calc} [gcm^{-3}]	1.887	1.763
Z	2	2
F(000) [e]	1048	1648
$\mu(Mo\text{-}K_\alpha)$ [cm^{-1}]	77.90	71.00
cryst. dim. [mm]	0.30 / 0.35 / 0.50	0.25 / 0.30 / 0.55
T [°C]	- 56	- 56
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	Θ-Θ	Θ-Θ
hkl range	+ 14 / ± 16 / ± 18	+ 18 / ± 18 / ± 22
measured reflections	8360	14128
unique reflections	7894	12747
observed reflections	7159	10595
R_{int}	0.0685	0.0537
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$
refined parameters	451	643
H-atoms (found/calc.)	- / 39	- / 49
absorption corr.:	empirical	empirical
T_{min} / T_{max}	0.6496 / 0.9984	0.7214 / 0.9970
R [a]	0.0260	0.0467
R_w [b]	0.0337	0.0621
weighting scheme [c]	l = 1.0000 / k = 0.000417	l = 1.0000 / k = 0.000601
ρ_{fin}(max/min) [$eÅ^{-3}$]	+ 1.53 / - 1.55	+ 2.78 / - 3.56

[a] $R = \sum||F_o|-|F_c||/\sum F_o|$. – [b] $R_w = \sqrt{\sum w(|F_o|-|F_c|)^2/\sum wF_o^2}$. – [c] $w = \dfrac{l}{\sigma^2(F_o) + kF_o^2}$.

1,2-Ethanedithiolato-tris[(triphenylphosphine)gold(I)] Tetrafluoroborate (**2**): Tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (0.52 g, 0.35 mmol) is dissolved in 10 ml of dichloromethane. In the presence of 0.10 g of sodium tetrafluoroborate (0.91 mmol) 0.020 ml of ethane-1,2-dithiol is added very slowly with stirring. After 2 h at room temperature, the clear yellow solution is concentrated under vacuum and pentane is added. The yellow precipitate is crystallized from CH_2Cl_2/Et_2O at room temperature. Colorless crystals, yield 0.41 g (100%), dec. temp. 169 °C. – ^1H NMR: δ = 1.76 (s, CH_2), 7.13–7.35 (m, Ph-*ortho*/*meta*), 7.40 (m, Ph-*para*). – $^{13}C\{^1H\}$ NMR: δ = 38.88 (s, CH_2), 129.01 (d, $^1J_{CP}$ = 49.64 Hz, Ph-*ipso*), 129.26 (d, $^3J_{CP}$ = 11.03 Hz, Ph-*meta*), 131.86 (s, Ph-*para*), 133.73 (d, $^2J_{CP}$ = 13.79 Hz, Ph-*ortho*). – $^{31}P\{^1H\}$ NMR (22 °C): δ = 36.15 (s, PPh_3); –30 °C: δ = 35.57; –60 °C: δ = 35.21. – MS (FAB): *m*/*z* (%) = 1468.8 (31.43) $[M^+]$, 459.1 (100) $[Ph_3PAu^+]$. – $C_{56}H_{49}Au_3BF_4P_3S_2$ (1556.77): calcd. C 43.21, H 3.17, Au 37.96; found C 42.80, H 3.25, Au 38.47.

Crystal Structure Determination: The samples were mounted in glass capillaries under nitrogen. Graphite-monochromated Mo-K_α radiation was used. The structures were solved by direct methods (SHELXTL-PC). The final cell parameters and specific data collection parameters are summarized in Table 1. Further details of the X-ray structure determinations have been deposited at Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the depository number CSD 59019.

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