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Terminally Bifurcated Tetraaurio-α,ω-bis(sulfonium) Salts as Building Blocks for Auriophilicity-Determined Coordination Polymers

Alexander Sladek and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching, Germany

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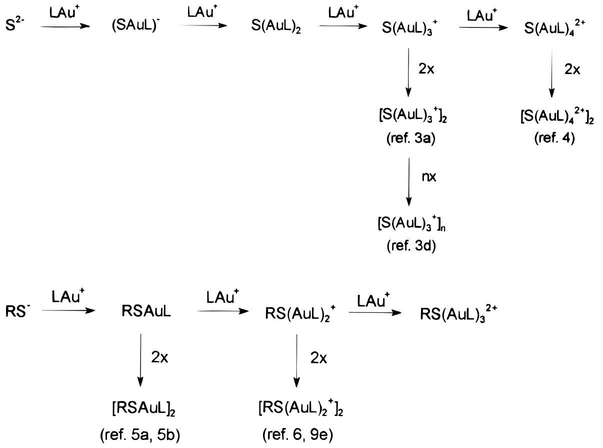
Treatment of α,ω-dithiols $HS(CH_2)_nSH$, $n = 4$ or 5, with tris[(triphenylphosphine)aurio]oxonium tetrafluoroborate affords the corresponding *S,S,S′,S′*-tetrakis[(triphenylphosphine)aurio]-α,ω-alkanediylbis(sulfonium) bis(tetrafluoroborates) of the type $\{[(Ph_3P)Au]_2S(CH_2)_nS[Au(PPh_3)]_2\}^{2+}2BF_4^-$. The crystal structure of the species with $n = 5$ has been determined by single crystal X-ray diffraction studies. In the lattice the unfolded dications are linked into chains through short double Au−Au contacts between the terminal bifurcated diauriosulfonium centers. The analogous reactions with (racemic) 1,2-dithioglycerol and 1,2,3-trithioglycerol also give tri- and tetranuclear complexes with a varying distribution of the metal atoms over the chalcogen(ium) centers. As again demonstrated in a single crystal X-ray diffraction study, the dications $\{HOCH_2HCS[(Ph_3P)Au]_2CH_2S[Au(PPh_3)]_2\}^{2+}$ of the *di*thioglycerol compound form only dimers through auriophilicity-determined pairing of the bifurcated ends, while the open ends are shielded by the dangling hydroxyl group. The *tri*nuclear complex of 1,2-*di*thioglycerol is fluxional in solution; the crystal structure has not been determined but is expected to be similar to that derived for the analogous dithioglycol complex. The tetranuclear, *tri*thioglycerol-based dications of $\{[(Ph_3P)Au]SCH_2CHS[Au(PPh_3)]CH_2S[Au(PPh_3)]_2\}^+BF_4^-$ are isolated in the lattice and feature an unsymmetrical complexation, which is an extension of the structure of the trinuclear dithioglycol analogue $\{(CH_2S)_2[Au(PPh_3)]_3\}^+$ with its strong *intra*molecular Au−Au contacts. A similar structure is proposed for the monocation $\{CH_2(CH_2S)_2[Au(PPh_3)]_3\}^+$ obtained from propane-1,3-dithiol. The structures of these cations are also fluxional in solution, however, as shown by variable-temperature NMR studies.

Introduction

Hydrogen sulfide and thiols are known to form tetra-, tri-, and dinuclear auriosulfonium complexes with interesting supramolecular structures.[1−6] The individual cations $\{S[Au(PR_3)]_3\}^+$ and $\{RS[Au(PR_3)]_2\}^+$ are associated into dimers or even polymers through short intermolecular Au−Au contacts (auriophilicity,[7] Scheme 1). These gold-rich sulfonium salts are thermally quite stable, not sensitive to air and moisture under standard conditions, and highly soluble in polar organic solvents. These properties qualify the compounds as substrates for electrochemical or electroless deposition of gold from solutions, for the reductive preparation of gold colloids (cluster solutions), and as gold drugs for chemotherapy,[8] where their role as component of equilibria has already been firmly established.[8h]

Scheme 1



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Most of the previous studies have been limited to derivatives of H_2S [or $(Me_3Si)_2S$] and of monofunctional thiols RSH, except for some recent investigations which also included dithiocatechol, dithioglycol, and dithioglycerol (BAL).[8h,9] We have therefore initiated a more systematic study of polynuclear gold(I) complexes of α,ω-alkanediyldithiols $HS(CH_2)_nSH$ with $n = 3$, 4, and 5 and of di- and trithioglycerols. It was anticipated that the corresponding terminally bifurcated disulfonium salts would show interesting aggregation to give either strong *intra*molecular Au−Au interactions or supramolecular structures based on *inter*molecular Au−Au contacts between the geminal SAu_2 units.

Regarding the preparation of the poly(aurio)sulfonium salts, the established literature method using tris[(phosphine)aurio]oxonium salts $[(R_3P)Au]_3O^+BF_4^-$ appeared to be the most convenient technique for the auration of thiols. (Phosphine)gold tetrafluoroborates $[(R_3P)Au]^+BF_4^-$ are more powerful aurating agents, which can even lead to hypercoordination of sulfur.[4] This was not within the scope of the present study, however, because the excessively aurated products are expected to be of a more limited stability and hence less suitable as sources for gold in or from solution under standard conditions.

Experimental Section

General Information. The experiments were carried out routinely under an atmosphere of dry and pure nitrogen. Glassware and solvents were dried and filled/saturated with nitrogen. NMR: Jeol GX 400 spectrometer; deuterated solvents with the usual standards. MS: Varian MAT 311A instrument (FAB, *p*-nitrobenzyl alcohol, or FD, dichloromethane solvent). The thiols were commercially available, except for trithioglycerol.[10] $[(Ph_3P)Au]_3O^+BF_4^-$ was prepared following the literature procedure.[11]

(Propane-1,3-dithiolato)tris[(triphenylphosphine)gold(I)] Tetrafluoroborate (1). A solution of $[(Ph_3P)Au]_3O^+BF_4^-$ (0.30 g, 0.20 mmol) in dichloromethane (10 mL) is treated with 1,3-propanedithiol (0.02 mL, 0.20 mmol) at ambient temperature with stirring. After 1 h a gray-white flaky precipitate is filtered off and the solvent is evaporated from the filtrate in a vacuum to leave a white powder (0.24 g, 75% yield). The product could not be crystallized. MS: $m/z = 1483.3$ [M^+, 17%], 721 [$\{(Ph_3P)_2Au\}^+$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 38.2$ [s]. $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 29.3$ [s, CH_2S], 46.0 [s, CH_2C], 129.0 [d, $J_{P,C} = 54.2$ Hz, C_{ipso}], 129.4 [d, $J = 11.0$, C_{meta}], 132.0 [d, $J = 2.8$, C_{para}], 133.8 [d, $J = 13.8$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): 2.13 [m, 2H, CH_2C], 3.14 [m, 4H, CH_2S], 7.31−7.50 [m, 45 H, H_{Ph}]. Anal. Calcd (Found) for $C_{57}H_{51}Au_3BF_4P_3S_2$ ($M_r = 1570.80$): C, 43.58 (43.77); H, 3.27 (3.28); Au, 37.62 (37.00).

(*n*-Butane-1,4-dithiolato)tetrakis[(triphenylphosphine)gold(I)] Bis(tetrafluoroborate) (2). A solution of the oxonium salt (above, 0.50 g, 0.34 mmol) in CH_2Cl_2 (10 mL) is treated with $NaBF_4$ (0.10 g, 0.91 mmol) and then with 1,4-butanedithiol (0.03 mL, 0.26 mmol) at ambient temperature with stirring. After 30 min a white flaky precipitate is removed by filtration and the filtrate layered at −20 °C with diethyl ether (20 mL). After 15 h clear colorless crystals are obtained (0.27 g, 49% yield), mp 165 °C (dec). MS (FD, CH_2Cl_2): $m/z = 1955.3$ [$(M - 1)^+$, 3.4%], 1408.2 [$\{(Ph_3P)Au\}_3S^+$, 100%]. MS (FAB): $m/z = 2043.4$ [$\{M + BF_4\}^+$, 10.5%], 720.4 [$\{(Ph_3P)_2Au\}^+$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 39.5$ [s]. $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 25 °C): 30.6 [s, CH_2S], 35.9 [s, CH_2C], 129.4 [d, $J_{P,C} = 51.5$ Hz, C_{ipso}], 129.45 [d, $J = 11.0$, C_{meta}], 131.9 [d, $J = 2.8$, C_{para}], 1323.7 [d, $J = 13.8$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): 1.85 [m, 4H, H_2C], 3.0 [m, 4H, CH_2C], 7.30−7.50 [m, 60H, H_{Ph}]. Anal. Calcd (Found) for $C_{76}H_{68}Au_4B_2F_8P_4S_2$ ($M_r = 2130.88$): C, 42.84 (43.01); H, 3.22 (3.20); Au, 36.97 (37.51).

(*n*-Pentane-1,5-dithiolato)tetrakis[(triphenylphosphine)gold(I)] Bis(tetrafluoroborate) (3). A solution of the oxonium salt (above, 0.29 g, 0.20 mmol) and $NaBF_4$ (0.1 g, 0.91 mmol) in CH_2Cl_2 (10 mL) is treated with 1,5-pentanedithiol (0.02 mL, 0.15 mmol) at room temperature with stirring. After 1 h a brown precipitate is removed by filtration and the filtrate layered with diethyl ether (30 mL) at −78 °C. After 12 h colorless crystals are isolated (0.15 g, 45% yield), mp 179 °C (dec). MS (FD, CH_2Cl_2): $m/z = 985.9$ [$M^{2+}/2$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 37.3$ [s]. $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 27.2$ [s, CH_2CCS], 32.3 [s, CH_2CS], 36.0 [s,CH_2S], 127.5 [d, $J_{P,C} = 60.7$ Hz, C_{ipso}], 129.8 [d, $J = 11.0$, C_{meta}], 132.6 [s, C_p], 133.9 [d, $J = 12.9$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): 1.66 [m, 2H, CH_2CCS], 1.87 [m, 4H, CH_2CS], 3.37 [m, 4H, CH_2S], 7.41−7.51 [m, 60H, H_{Ph}]. Anal. Calcd (Found) for $C_{77}H_{70}Au_4B_2F_8P_4S_2$ ($M_r = 2144.91$): C, 43.12 (42.78); H, 3.29 (3.28); Au, 36.73 (37.10).

(3-Hydroxypropane-1,2-dithiolato)tetrakis[(triphenylphosphine)gold(I)] Bis(tetrafluoroborate) (4). A solution of the oxonium salt (above, 0.49 g, 0.33 mmol) and $NaBF_4$ (0.10 g, 0.91 mmol) in dichloromethane (10 mL) is treated with racemic 2,3-dithioglycerol (0.025 g, 0.25 mmol) at ambient temperature with stirring. After 75 min the reaction mixture is filtered and the solvent is removed from the filtrate. The residue is treated with ethanol and filtered, the filtrate again brought to dryness in a vacuum, and the filtrate redissolved in dichloromethane. This solution is layered with diethyl ether to crystallize the product as colorless needles (0.12 g, 23% yield), mp 165 °C (dec). MS (FAB): $m/z = 1498.9$ [$\{M-AuPPh_3\}^+$, 15%], 979.0 [M^{2+}, 1.3%], 720.9 [$\{(Ph_3P)_2Au\}^+$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 34.6$ [s]; −30 °C, 34.0 [s], −60 °C: 33.6 [s]. $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 37.4$ [s, CH_2S], 56.7 [s, CH], 67.7 [s, CH_2-OH], 127.6 [d, $J_{P,C} = 59.8$ Hz, C_{ipso}], 129.7 [d, $J = 11.9$, C_{meta}], 130.1 [s, C_{para}], 133.8 [d, $J = 13.8$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.77$ [s, 1H, OH], 3.79−3.95 [m, 5H, CH_2/CH], 7.20−7.71 [m, 60H, H_{Ph}]. Anal. Calcd (Found) for $C_{75}H_{66}Au_4B_2F_8OP_4S_2$ ($M_r = 2132.86$): C, 42.24 (41.84); H, 3.12 (3.14); Au, 36.94 (37.44).

(3-Hydroxypropane-1,2-dithiolato)tris[(triphenylphosphine)gold(I)] Tetrafluoroborate (5). A solution of the oxonium salt (above, 0.44 g, 0.33 mmol) in CH_2Cl_2 (10 mL) is treated with racemic 2,3-dithioglycerol (0.03 mL, 0.33 mmol) at ambient temperature with stirring. After 60 min the reaction mixture is layered with diethyl ether (40 mL). A precipitate is formed, which is filtered off after 12 h and taken up in ethanol. The solution is filtered and the filtrate brought to dryness in a vacuum to leave a white solid (0.20 g, 43% yield). The product could not be crystallized. MS (FAB): $m/z = 1498.2$ [M^+, 20%], 1408.3 [$\{S(AuPPh_3)_3\}^+$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 35.7$ [s]; −55 °C, 34.7 [s]. $\{^1H\}^{13}C$ NMR ($CDCl_3$, 25 °C): $\delta = 40.1$ [s, CH_2S], 57.0 [s, CH], 68.1 [s, CH_2O], 128.8 [d, $J_{P,C} = 57.3$ Hz, C_{ipso}], 129.3 [d, $J = 11.9$, C_{meta}], 131.9 [s, C_{para}], 133.8 [d, $J = 13.7$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 1.85$ [s, 1H, OH], 3.90−4.10 [m, 5H, CH_2/CH], 7.15−7.57 [m, 45H, H_{Ph}]. Anal. Calcd (Found) for $C_{57}H_{51}Au_3BF_4OP_3S_2$ ($M_r = 1586.79$): C, 43.15 (43.54); H, 3.24 (3.25); Au, 37.24 (38.40).

(Propane-1,2,3-trithiolato)tetrakis[(triphenylphosphine)gold(I)] Tetrafluoroborate (6). A solution of the oxonium salt (above, 0.52 g, 0.35 mmol) in CH_2Cl_2 (10 mL) is treated with trithioglycerol (0.030 mL, 0.26 mmol) at room temperature with stirring. After 1 h the reaction mixture is layered with diethyl ether (20 mL) at −78 °C. A brown oil and yellow crystals are formed (12 h). The crystals are separated by decantation (0.35 g, 65% yield), mp 198 °C (dec). MS (FAB): $m/z = 1973.5$ [$\{M - 1\}^+$, 4.3%], 458.8 [$\{Ph_3PAu\}^+$, 100%]. $\{^1H\}$ ^{31}P NMR ($CDCl_3$, 25 °C): $\delta = 35.6$ [s]. $\{^1H\}$ ^{13}C NMR ($CDCl_3$, 25 °C): $\delta = 37.1$ [s, CH_2], 59.6 [s, CH], 129.1 [d, $J_{P,C} = 11.0$ Hz, C_{meta}], 129.7 [s, $J = 55.2$, C_{ipso}], 132.6 [s, C_{para}], 133.8 [d, $J = 13.8$, C_{ortho}]. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 3.66$ [m, 4H, CH_2], 3.74 [m, 1H, CH], 7.17−7.38 [m, 60H, H_{Ph}]. Anal. Calcd (Found) for $C_{75}H_{65}Au_4BF_4P_4S_3$ ($M_r = 2061.11$): C, 43.71 (44.07); H, 3.18 (3.19); Au, 38.23 (37.72).

Crystal Structure Determinations. Suitable crystals of compounds **3**, **4**, and **6** were sealed under argon at dry ice temperature into glass

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Table 1. Crystallographic Data for Compounds **3**, **4**·CH_2Cl_2, and **6**·CH_2Cl_2·$(CH_3CH_2)_2O$

	3	**4**·CH_2Cl_2	**6**·CH_2Cl_2·$(CH_3CH_2)_2O$
empirical formula	$C_{77}H_{70}Au_4B_2F_8P_4S_2$	$C_{75}H_{66}Au_4B_2F_8OP_4S_2$·$CH_2Cl_2$	$C_{75}H_{65}Au_4BF_4P_4S_3$·$CH_2Cl_2$·$(CH_3CH_2)_2O$
formula weight	2144.81	2217.69	2220.05
crystal system	triclinic	triclinic	triclinic
space group (No.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	12.869(2)	13.420(1)	10.934(1)
b [Å]	14.365(2)	14.558(2)	18.502(2)
c [Å]	22.559(3)	20.857(3)	20.393(3)
α [deg]	78.99(1)	108.55(1)	77.40(1)
β [deg]	89.24(1)	94.78(1)	79.07(2)
γ [deg]	64.81(1)	96.14(1)	83.75(1)
V [Å^3]	3693.40	3811.05	3943.31
ρ_{calc} [g cm^{-3}]	1.942	1.933	1.870
Z	2	2	2
μ(Mo Kα) [cm^{-1}]	81.80	79.50	77.00
T [°C]	−68	−68	−62
radiation	Mo Kα	Mo Kα	Mo Kα
scan	ω	$\theta-\theta$	$\theta-\theta$
hkl range	±15/±17/+26	±16/±17/+25	±13/+22/±25
measured reflections	12 848	14 856	14 656
unique reflections	11 082	12 810	13 104
observed reflections	8581	9902	10 781
$F_o \geq$	$4\sigma(F_o)$	$4\sigma(F_o)$	$4\sigma(F_o)$
refined parameters	651	679	713
R^a	0.0560	0.0539	0.0400
$R_w{}^b$	0.0704	0.0583	0.0418
ρ_{fin}(max/min) [e Å^{-3}]	+1.83/−2.35	+2.16/−2.03	+1.70/−1.30
abs corr	empirical	empirical	empirical
T_{min}/T_{max}	0.2050/0.9998	0.5399/0.9994	0.5226/0.9994
weighting scheme^c	$l = 1.0000/k = 0.001147$	unit weights	$l = 1.0000/k = 0.000238$

^{a} $R = \sum||F_o| - F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - F_c|)^2/\sum wF_o{}^2]^{1/2}$. ^{c} $w = l/\sigma^2(F_o) + kF_o{}^2$.

capillaries and examined directly on the diffractometer. Data were corrected for Lorentz, polarization, and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations. The thermal motion was treated anisotropically for all non-hydrogen atoms, except for seven phenyl carbon atoms of compound **3** and except for the disordered CH_2OH group of compound **4**. All calculated hydrogen atoms were treated isotropically. More detailed information on solution and refinement procedures is given in the Supporting Information, as are the atomic coordinates.

Results and Discussion

The reaction of *propane-1,3-dithiol* with equivalent amounts of tris[(triphenylphosphine)aurio]oxonium tetrafluoroborate in dichloromethane at room temperature leads, in high yield, to a colorless microcrystalline precipitate, which was shown to be the trinuclear complex **1** formulated in eq 1. The product was identified by elemental analysis, fast atom bombardment mass spectrometry, and NMR spectroscopy (Experimental Section). On the basis of these data, a structure is proposed for **1**, which resembles that of the analogous products obtained from dithioglycerol and dithiocatechol. No single crystals suitable for diffraction studies could be obtained.

$$HS(CH_2)_3SH + [(Ph_3P)Au]_3O^+BF_4{}^- \rightarrow H_2O + \{[S(CH_2)_3S][Au(PPh_3)]_3\}^+BF_4{}^- \ (\mathbf{1}) \quad (1)$$

Under similar reaction conditions, *butane-1,4-dithiol* was converted into a tetranuclear complex **2**, which was obtained in moderate yield as colorless crystals upon layering of the dichloromethane solutions with diethyl ether at −78 °C (eq 2). The composition was confirmed by standard analytical techniques, but none of the single crystals had the quality necessary for a structure determination. The structure proposed tentatively for this product is based on the findings for the pentane homologue (**3**, below).

$$HS(CH_2)_4SH + [(Ph_3P)Au]_3O^+BF_4{}^- \rightarrow H_2O + \{[(Ph_3P)Au]_2[S(CH_2)_4S][Au(PPh_3)]_2\}^{2+}(BF_4{}^-)_2 \ (\mathbf{2}) \quad (2)$$

Pentane-1,5-dithiol gave the analogous tetranuclear derivative (**3**) in moderate yield (eq 2), which showed physical and spectroscopic properties very similar to those of compound **2**. Single crystals were readily obtained, which were shown to be triclinic, space group $P\bar{1}$ (No. 2, Int. Tables) with two formula units in the unit cell (Table 1). The lattice is composed of isolated independent tetrafluoroborate anions and chains of cations. In the individual units of these chains the five-membered hydrocarbon moiety is unfolded, with a bifurcated $S(AuL)_2$ function at either end (L = PPh_3, Figure 1).

The diauriosulfonium groups are in close contact with the corresponding units of neighboring molecules in an inverse orientation to form only slightly distorted squares of gold atoms around crystallographic centers of inversion (Figure 2). This auriophilicity-based pairing of bifurcated units is known from the structural chemistry of diaurated monosulfonium salts but is observed here for the first time for α,ω-difunctional substrates. Owing to the double fixation (two Au−Au contacts at either end), the supramolecular structures of **2** and **3** are probably quite robust, with estimated enthalpies of aggregation of at least 15 kcal per pair of connecting units.[12] Note that this aggregation occurs between cationic units (and thus against repulsive Coulomb forces) and that the gold atoms become nearest neighbors, and not gold and sulfur. These are common criteria for auriophilicity phenomena.

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[12] (a) Dziwok, K.; Lachmann, J.; Wilkinson, D. L.; Müller, G. *Chem. Ber.* **1990**, *123*, 423. (b) Schmidbaur, H.; Dziwok, K.; Grohmann, A.; Müller, G. *Chem. Ber.* **1989**, *122*, 893. (c) Schmidbaur, H.; Graf, W.; Müller, G. *Angew.Chem.* **1988**, *100*, 439; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416.

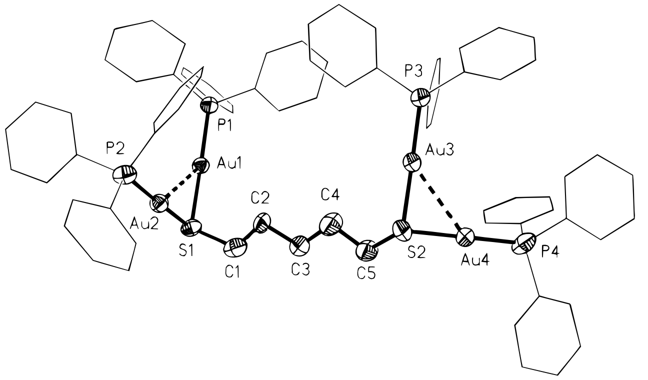


Figure 1. Structure of the dication in the crystal of $\{[(Ph_3P)Au]_2S(CH_2)_5S[Au(PPh_3)]_2\}^{2+}(BF_4^-)_2$ **3** (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity). Selected distances [Å] and angles [deg]: Au1−Au2, 3.224(1); Au1−S1, 2.330(3); Au1−P1, 2.267(3); Au2−S1, 2.314(5); Au2−P2, 2.259(5); Au3−Au4, 3.071(1); Au3−S2, 2.331(3); Au3−P3, 2.261(4); Au4−S2, 2.328(5); Au4−P4, 2.252(7); Au1−S1−Au2, 87.9(1); Au1−S1−C1, 109.9(5); Au2−S1−C1, 105.4(7); P1−Au1−S1, 176.0(2); P2−Au2−S1, 177.0(1); Au3−S2−Au4, 82.5(1); Au3−S2−C5, 107.4(5); Au4−S2−C5, 106.2(8); P3−Au3−S2, 179.1(2); P4−Au4−S2, 178.0(2).

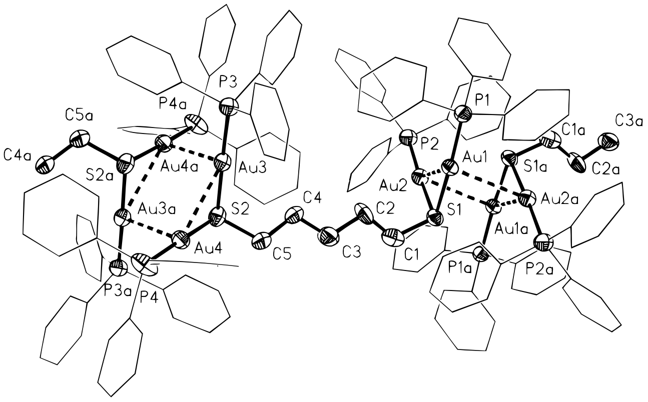


Figure 2. Part of a chain of $\{[(Ph_3P)Au]_2S(CH_2)_5S[Au(PPh_3)]_2\}^{2+}$ dications in the lattice of **3** (ORTEP, carbon atoms and hydrogen atoms omitted for clarity). Selected distances [Å] and angles [deg]: Au1−Au2a, 3.225(1); Au3−Au4a, 3.349(1); Au2−Au1−Au2a, 86.5(1); Au4−Au3−Au4a, 90.7(1).

Racemic *1,2-dithioglycerol* also affords a tetranuclear auration product **4** (eq 3), which could be isolated as colorless single crystals of limited stability in low yield. The X-ray diffraction analysis revealed a structure in which the dications are associated only into dimers (Figure 3). The terminal bifurcated $S(AuL)_2$ units form centrosymmetrical tetranuclear units, while those at the central carbon atom of the glycerol are not engaged in intermolecular contacts. Such contacts are probably prevented by the neighboring CH_2OH group, the position of which is disordered in the crystal.

$$HOCH_2(CHSH)CH_2SH + [(Ph_3P)Au]_3O^+BF_4^- \rightarrow H_2O + \{HOCH_2HCS[(Ph_3P)Au]_2CH_2S[Au(PPh_3)]_2\}^{2+}(BF_4^-)_2\ (\mathbf{4}) \qquad (3)$$

With a different stoichiometry of the reagents, a *tri*nuclear complex of racemic 1,2-dithioglycerol can also be obtained (**5**, eq 4). The product has been identified by standard analytical and spectroscopic data, but it could not be crystallized. Variable-temperature ^{31}P NMR spectra showed that the compound is fluxional in solution referring to a rapid site exchange of the gold phosphine units at the sulfur centers. This process appears to be rapid on the NMR time scale in solution even at −55 °C, where a single sharp resonance is obtained. The ground state structure is assumed to be similar to that of the trinuclear dithioglycol complex (**B**, below).

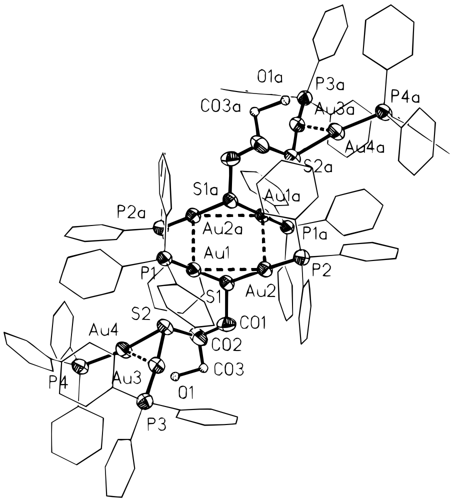


Figure 3. A pair of dications $\{HOCH_2HCS[(Ph_3P)Au]_2CH_2S[Au(PPh_3)]_2\}^{2+}$ in the tetrafluoroborate salt **4** (ORTEP, except for phenyl carbon atoms and the CH_2OH group; hydrogen atoms omitted for clarity). Selected distances [Å] and angles [deg]: Au1−Au2, 3.101(1); Au1−S1, 2.357(3); Au1−P1, 2.275(4); Au2−S1, 2.331(4); Au2−P2, 2.261(5); Au3−Au4, 3.040(1); Au3−S2, 2.331(4); Au3−P3, 2.254(4); Au4−S2, 2.316(4); Au4−P4, 2.241(5); Au1−Au2a, 3.287(1); Au1−S1−Au2, 82.8(1); Au1−S1−C01, 104.6(5); Au2−S1−C01, 105.6(6); P1−Au1−S1, 172.8(2); P2−Au2−S1, 175.8(1); Au3−S2−Au4, 81.7(1); Au3−S2−C02, 108.0(6), Au4−S2−C02 110.0(6), P3−Au3−S2 174.5(1), P4−Au4−S2 170.1(2); Au2−Au1−Au2a, 87.8(1).

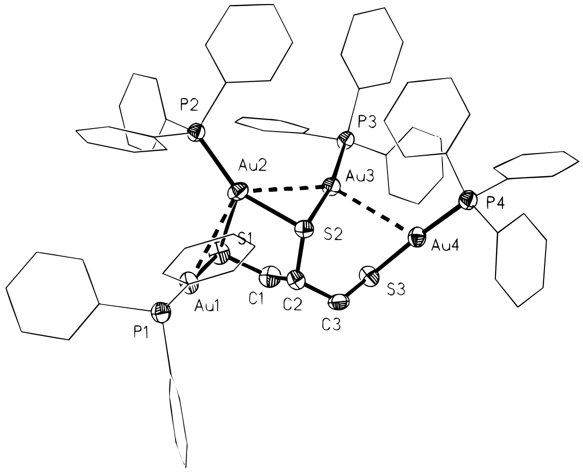
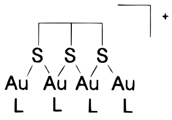


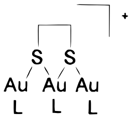
Figure 4. Structure of the cation in the crystal of $\{[(Ph_3P)Au]SCH_2CHS[Au(PPh_3)]CH_2S[Au(PPh_3)]_2\}^+BF_4^-$ **6** (ORTEP, except for phenyl carbon atoms; hydrogen atoms omitted for clarity). Selected distances [Å] and angles [deg]: Au1−Au2, 3.201(1); Au2−Au3, 3.227(1); Au3−Au4, 3.178(1); Au1−S1, 2.296(3); Au2−S1, 2.597(2); Au2−S2, 2.399(2); Au3−S2, 2.328(2); Au4−S3, 2.285(2); Au1−P1, 2.247(3); Au2−P2, 2.248(2); Au3−P3, 2.255(2); Au4−P4, 2.254(2); Au1−S1−Au2, 81.5(1); Au1−S1−C1, 103.0(3); Au2−S1−C1, 97.1(3); Au2−S2−C2, 103.8(3); P1−Au1−S1, 175.5(1); P2−Au2−S1, 123.7(1); P2−Au2−S2, 149.1(1); Au2−S2−Au3, 86.1(1); Au3−S2−C2, 102.7(3); P3−Au3−S2, 169.3(1); Au4−S3−C3, 101.7(3); P4−Au4−S3, 176.8(1).

$$HOCH_2(CHSH)CH_2SH + [(Ph_3P)Au]_3O^+BF_4^- \rightarrow H_2O + \{[HOCH_2(CHS)CH_2S][Au(PPh_3)]_3\}^+BF_4^-\ (\mathbf{5}) \qquad (4)$$

Trithioglycerol forms a tetranuclear complex in good yield (**6**, eq 5) with a distinctly unsymmetrical distribution of the four metal atoms over the three thiolate donor centers, as determined by X-ray diffraction (Figure 4). Note that a symmetrical structure (**A**) is possible for this cation (with a mirror plane or a 2-fold axis), but this is not what is found in the lattice of the tetrafluoroborate salt. However, the structure is reminiscent of the configuration described for the trinuclear dithioglycol complex (**B**).



A



B

$$\mathrm{HSCH_2(CHSH)CH_2SH + [(Ph_3P)Au]_3O^+BF_4^- \rightarrow H_2O + \{[SCH_2(CHS)CH_2S][Au(PPh_3)]_4\}^+BF_4^-}\ (\mathbf{6}) \quad (5)$$

As shown by variable-temperature NMR spectroscopy, the structure of **5** is not rigid in solution (dichloromethane), but has to be taken as fluxional. The rapid site exchange of the AuL units leads to pseudosymmetry on the NMR time scale at ambient temperature, rendering all phosphine units equivalent. The two glycerol CH_2 groups are also found to be pseudoequivalent under these conditions.

Conclusions. The present study has shown that polythiol molecules can readily be converted into polynuclear [(phosphine)aurio]sulfonium salts with mono- or diaurated sulfur centers. The distribution of the gold atoms can be symmetrical and/or asymmetrical, and in solution a rapid site exchange can lead to a redistribution of the metal atoms over the sulfur donor sites. The ground state structures, as determined by crystal structure analysis, feature distinct intramolecular gold−gold contacts at the diaurated sulfonium centers or between $S(AuL)_2^+$- and S(AuL) units. In sterically favorable cases two of the bifurcated terminal $S(AuL)_2^+$ units can aggregate through double Au−Au contacts to form novel auriophilicity-determined supramolecular systems, as first detected here for compound **3**. There is reason to believe that other classes of polynuclear gold(I) complexes will give rise to similar phenomena.

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Supporting Information Available: Tables of atomic coordinates and thermal parameters, hydrogen atom parameters, and bond distances and angles (78 pages). Ordering information is given on any current masthead page.

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