

Gold Clustering at the Terminal Functions of Long-Chain Thiols and Amines

José M. López-de-Luzuriaga, Alexander Sladek, Annette Schier, and Hubert Schmidbaur*

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

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Treatment of 1,6-hexanedithiol with $4/3$ mol equiv of tris[(triphenylphosphino)aurio(I)]oxonium tetrafluoroborate and sodium tetrafluoroborate affords (*n*-hexane-1,6-dithiolato)tetrakis-[(triphenylphosphine)gold(I)] bis(tetrafluoroborate) (**1**). The analogous reactions with β -mercaptoethylamine, HS(CH₂)₂NH₂, 1,4-diaminobutane, H₂N(CH₂)₄NH₂, and *n*-butyl- and *n*-octylamine, CH₃(CH₂)_{*n*}NH₂ (*n* = 3 or 7), give the corresponding penta- (**2**), hexa- (**3**), and trinuclear (**4**, **5**) complexes, respectively. The crystal structures of compounds **3** and **5** have been determined by single-crystal X-ray diffraction studies. In the hexanuclear complex **3**, three gold atoms are bonded to each nitrogen, putting each of these atoms at the apex of an NAu₃ pyramid. There are no intra- or intermolecular interactions between the gold centers of different nitrogen atoms. The trinuclear complex **5** features the unfolded aliphatic chain at the apex of such a pyramid. In both compounds the gold atoms show close contacts of 3.0 ± 0.1 Å, indicating significant bonding, which is probably the main driving force for the clustering of seemingly closed-shell (d¹⁰) gold(I) metal atoms.

Introduction

For many decades it has been explicitly or tacitly assumed that gold surfaces are completely inert toward virtually all chemicals except for the most aggressive oxidants. Recent studies have shown very conclusively, however, that gold surfaces are covered rapidly by monolayers of thiolate units when exposed to either thiol-containing solutions or to thiol vapors.¹

This chemisorption leads to what is addressed as self-assembled monolayers in which the thiols are anchored at the top layer of gold atoms of the bulk metal through their sulfur atom. Evolution of hydrogen is believed to occur, and there is ample physical evidence that the thiols indeed end up as thiolate groups. This model then requires the presence of at least 1 mol equiv of gold(I) at or close to the surface. The resulting efficient coverage of the surface by either hydrophilic or hydrophobic thiolates and its “engineering” are the basis for a variety of applications in the realm of what may be classified as two-dimensional nanotechnology.

While the knowledge of the processes involved on the macroscopic level has advanced very rapidly,^{2–6} there is still considerable debate about the nature of the chemisorption on the molecular level. A key question is the positioning of the sulfur atom on either only one gold atom, as a bridge between two gold atoms, or in the hollow sites between a triangle or square of gold atoms, depending on the crystallographic cut through the gold lattice (111, 100, etc.).

We have recently been able to isolate molecular and cationic species in which the sulfur atoms of thiols are the nucleation centers for up to three gold atoms resembling the various possible modes of interaction between anionic [RS][–] and cationic [LAu]⁺ units.⁷ This work has now been extended to include longer-chain and bis-terminal thiols.

Since there is also as yet limited evidence that amines may show similar anchoring behavior at gold surfaces,⁸ some long-chain amines and diamines and a mercapto–amine have also been considered.

Experimental Section

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 400 spectrometer; deuterated solvents with the usual standards. MS: Varian MAT 311A instrument (FAB, *p*-nitrobenzyl alcohol, or FD, dichloromethane solvent). The thiols, amines, and the thiol–amine were commercially available. [(Ph₃P)Au]₃O⁺BF₄[–] was prepared by following the literature procedure.⁹

Hexane-1,6-diylbis{[bis(triphenylphosphino)aurio(I)]-sulfonium} Bis(tetrafluoroborate) (1). A solution of HS(CH₂)₆SH (16.1 μL, 0.10 mmol) in dichloromethane (10 mL) was treated with [(Ph₃P)Au]₃O⁺BF₄[–] (0.20 g, 0.135 mmol) and NaBF₄. After 1 h of stirring a small amount of solid was filtered off, the solvent was evaporated from the filtrate in a vacuum to a volume of ca. 5 mL, and diethyl ether was added to precipitate complex **1** as a white solid (0.108 g, 50% yield). The product could not be crystallized from CH₂Cl₂ or CHCl₃ upon layering with pentane or hexane. MS: *m/z* = 992.1 [M⁺, 25.7%], 1409.0 [S(AuPPh₃)₃⁺, 100%]. ³¹P{¹H} NMR (CDCl₃, –60 °C): δ = 34.4 [s]. ¹H NMR (CDCl₃, –60 °C): 1.50 [m, 4H, CH₂], 1.79 [m, 4H, CH₂], 3.32 [m, 4H, CH₂S], 7.27–7.53 [m, 60H, H_{Ph}]. Anal. Calcd (found) for C₇₈H₇₂Au₄B₂F₈P₄S₂ (*M_r* = 2158.93): C, 43.57 (43.40); H, 3.18 (3.36); S, 2.75 (2.97).

[2-{Bis[(triphenylphosphino)aurio(I)]sulfonio}ethyl]{tris-[(triphenylphosphino)aurio(I)]ammonium Bis(tetrafluoroborate) (2). To a suspension of HS(CH₂)₂NH₂ (0.018 g, 0.24 mmol) in

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dichloromethane (10 mL) was added $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+\text{BF}_4^-$ (0.60 g, 0.405 mmol) and a small amount of NaBF_4 . After the suspension was stirred for 1 h, the precipitate was filtered off and the solvent was evaporated in a vacuum. Addition of diethyl ether (15 mL) gave a yellow precipitate (0.39 g, 64% yield). The product also could not be crystallized (see 1). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): $\delta = 34.9$ [s, 2P, PAuS], 29.1 [s, 3P, PAuN]. ^1H NMR (CDCl_3 , 25 °C): 3.78 [m, 2H, CH_2N], 4.75 [m, 2H, CH_2S], 7.16–7.38 [m, 75H, H_{Ph}]. Anal. Calcd (found) for $\text{C}_{92}\text{H}_{79}\text{Au}_5\text{B}_2\text{F}_8\text{NP}_5\text{S}$ ($M_r = 2544.02$): C, 43.06 (43.40); H, 3.09 (3.13); N, 0.50 (0.55), S, 1.51 (1.26).

Butane-1,4-diybis{tris[(triphenylphosphino)aurio(I)]-ammonium} Bis(tetrafluoroborate) (3). A solution of $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$ (0.01 g, 0.12 mmol) in CHCl_3 (10 mL) was treated with $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+\text{BF}_4^-$ (0.35 g, 0.24 mmol) with stirring. After 3 h the solvent was evaporated in a vacuum, and addition of diethyl ether (15 mL) led to the precipitation of a white solid (0.289 g, 80% yield). A chloroform solution (5 mL) of this product was layered with diethyl ether (30 mL) at room temperature. After 24 h colorless crystals were isolated. MS: $m/z = 1419.5$ [M^+ , 20.9%], 1190.1 [$(\text{M} - \text{AuPPh}_3)^{2+}$, 100%]. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): $\delta = 29.0$ [s]. ^1H NMR (CDCl_3 , 25 °C): 2.16 [m, 4H, CH_2C], 4.26 [m, 4H, CH_2N], 7.21–7.45 [m, 90H, H_{Ph}]. Anal. Calcd (found) for $\text{C}_{112}\text{H}_{98}\text{Au}_6\text{B}_2\text{F}_8\text{N}_2\text{P}_6$ ($M_r = 3013.28$): C, 44.10 (44.60); H, 3.17 (3.27); N, 0.70 (0.90).

n-Butyltris[(triphenylphosphino)aurio(I)]ammonium Tetrafluoroborate (4). To a dichloromethane solution (20 mL) of $\text{CH}_3(\text{CH}_2)_3\text{NH}_2$ (10 μL , 0.10 mmol) was added $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+\text{BF}_4^-$ (0.15 g, 0.10 mmol). After 2 h of stirring the solvent was completely removed in a vacuum. Addition of ethanol (3 mL) and diethyl ether (15 mL) gave complex 4 as a white precipitate (0.106 g, 69% yield). The methods used for crystal growth with compound 3 were not successful for this complex. MS: $m/z = 1448.4$ [M^+ , 48.6%], 459.3 [Ph_3PAu^+ , 100%]. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): $\delta = 29.1$ [s]. ^1H NMR (CDCl_3 , 25 °C): 0.92 [t, $J = 7.4$ Hz, 3H, CH_3], 1.60 [m, 2H, CH_2], 1.91 [m, 2H, CH_2], 4.21 [m, 2H, CH_2N], 7.12–7.46 [m, 45H, H_{Ph}]. Anal. Calcd (found) for $\text{C}_{58}\text{H}_{54}\text{Au}_3\text{BF}_4\text{NP}_3$ ($M_r = 1535.70$): C, 45.17 (45.36); H, 3.47 (3.54); N, 0.80 (0.90).

n-Octyltris[(triphenylphosphino)aurio(I)]ammonium Tetrafluoroborate (5). To a dichloromethane solution (20 mL) of $\text{CH}_3(\text{CH}_2)_7\text{NH}_2$ (12 μL , 0.13 mmol) was added $[(\text{Ph}_3\text{P})\text{Au}]_3\text{O}^+\text{BF}_4^-$ (0.20 g, 0.13 mmol). After 4 h of stirring the solvent was evaporated in a vacuum. Addition of diethyl ether (15 mL) led to the precipitation of complex 5 as a white solid (0.107 g, 52% yield). MS: $m/z = 1504.9$ [M^+ , 32.0%], 459.3 [Ph_3PAu^+ , 100%]. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): $\delta = 29.1$ [s]. ^1H NMR (CDCl_3 , 25 °C): 0.82 [m, 3H, CH_3], 1.21 [m, 8H, CH_2], 1.58 [m, 2H, CH_2], 1.91 [m, 2H, CH_2], 4.21 [m, 2H, CH_2N], 7.25–7.48 [m, 45H, H_{Ph}]. Anal. Calcd (found) for $\text{C}_{62}\text{H}_{62}\text{Au}_3\text{BF}_4\text{NP}_3$ ($M_r = 1592.03$): C, 46.37 (46.77); H, 3.87 (3.92); N, 0.76 (0.88).

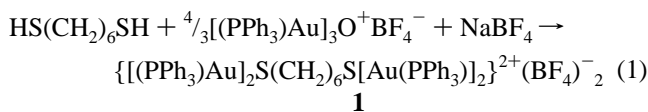
Crystal Structure Determinations. Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) with the ω/θ scan mode at -68 °C. An L_p correction was applied, and intensity data were corrected for decay [-12.5% (5) and -41.6% (3)] and absorption effects [ψ -scans, $T_{\text{min}}/T_{\text{max}} = 0.72/0.99$ (5), $0.79/0.99$ (3)]. The structures were solved by Patterson methods and completed by full-matrix least-squares techniques against F^2 .

Data for compound 5 • Et_2O : $\text{C}_{66}\text{H}_{72}\text{Au}_3\text{BF}_4\text{NOP}_3$, $M_r = 1665.87$, triclinic, $a = 12.236(1)$ Å, $b = 14.423(1)$ Å, $c = 19.644(2)$ Å, $\alpha = 101.99(1)^\circ$, $\beta = 105.82(1)^\circ$, $\gamma = 101.34(1)^\circ$, space group $P\bar{1}$ (No. 2), $Z = 2$, $D_{\text{calc}} = 1.761$ g cm^{-3} , $F(000) = 1612$ e, $\mu(\text{Mo } K\alpha) = 71.6$ cm^{-1} . A total of 12224 intensity data were measured up to $(\sin \theta/\lambda)_{\text{max}} = 0.64$ Å $^{-1}$, of which 11 741 independent structure factors were used for refinement. All non-H atoms were refined with anisotropic displacement parameters, except for those of the solvent diethyl ether. H atoms were placed in idealized calculated positions and allowed to ride on their carbon atoms. The function minimized was $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, with $w = 1/\sigma^2(F_o^2) + (ap)^2 + bp$ and $p = (F_o^2 + 2F_c^2)/3$ ($a = 0.0407$, $b = 4.86$). The final R and R_w values were 0.0423 [based on $F \geq 4\sigma(F)$] and 0.0819, respectively, for 672 refined parameters. Residual electron densities: $+2.032/-1.533$ e Å $^{-3}$, located around the gold atoms.

Data for compound 3 • 3CHCl_3 : $\text{C}_{115}\text{H}_{101}\text{Au}_6\text{B}_2\text{Cl}_9\text{F}_8\text{N}_2\text{P}_6$, $M_r = 3371.27$, triclinic, $a = 10.383(1)$ Å, $b = 18.617(1)$ Å, $c = 19.320(1)$ Å, $\alpha = 76.68(1)^\circ$, $\beta = 84.12(1)^\circ$, $\gamma = 78.33(1)^\circ$, space group $P\bar{1}$ (No. 2), $Z = 1$, $D_{\text{calc}} = 1.576$ g cm^{-3} , $F(000) = 1604$ e, $\mu(\text{Mo } K\alpha) = 64.6$ cm^{-1} . A total of 13024 intensity data were measured up to $(\sin \theta/\lambda)_{\text{max}} = 0.62$ Å $^{-1}$, of which 12 324 independent structure factors were used for refinement. All non-H atoms of the dication were refined with anisotropic displacement parameters. Due to disorder, the non-H atoms of the solvent molecules were treated isotropically, with the H atoms neglected. The BF_4 anions were included with fixed isotropic contributions. H atoms of the dication were placed in idealized calculated positions and allowed to ride on their carbon atoms. The function minimized was $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, with $w = 1/\sigma^2(F_o^2) + (ap)^2 + bp$ and $p = (F_o^2 + 2F_c^2)/3$ ($a = 0.1627$, $b = 37.87$). The final R and R_w values were 0.0777 [based on $F \geq 4\sigma(F)$] and 0.2146, respectively, for 640 refined parameters. Residual electron densities: $+4.110/-2.913$ e Å $^{-3}$, located around gold atoms.

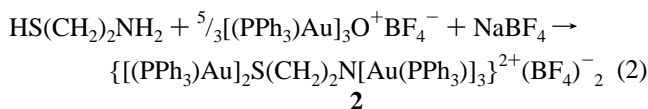
Results

Preparation, Properties, and Spectroscopic Data of the Compounds. The reaction of hexane-1,6-dithiol with tris[(triphenylphosphino)aurio]oxonium tetrafluoroborate and sodium tetrafluoroborate in dichloromethane at room temperature leads to the tetranuclear complex formulated in eq 1. The



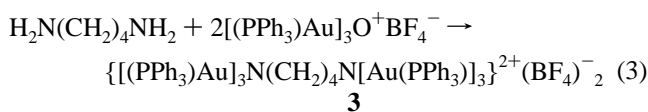
product was identified by elemental analysis, field desorption mass spectrometry and NMR spectroscopy (Experimental Section). The proposed structure is analogous to that of the previously reported complex with a shorter C_5 chain.¹⁰ No single crystals suitable for diffraction studies could be obtained.

Following the same procedure, cysteamine ((2-mercaptoethyl)amine) can be converted into the pentanuclear product 2, which was obtained as a yellow solid (eq 2). The composition



of compound 2 was confirmed by standard analytical techniques, and the proposed structure is based on the NMR data. The ^{31}P NMR spectrum shows two singlets at $\delta = 34.9$ (2 P) and 29.1 ppm (3 P), which are in accordance with the chemical shifts observed for $\text{Au}(\text{PPh}_3)$ groups bonded to sulfonium or ammonium centers, respectively, in compounds previously reported.^{7,10,11–15}

Treatment of 1,4-diaminobutane with tris[(triphenylphosphino)aurio]oxonium tetrafluoroborate under similar reaction conditions afforded the hexanuclear complex 3 in good yield (eq 3). The compound was identified by elemental analysis



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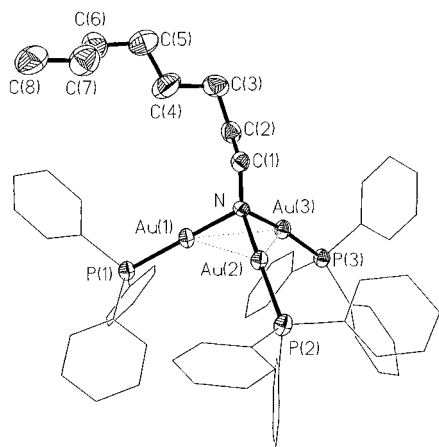
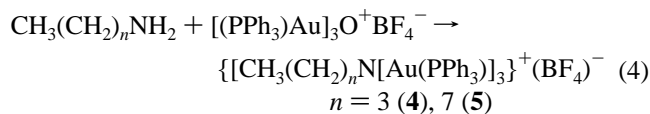


Figure 1. Molecular structure of the cation of complex **5** with atomic numbering (ORTEP, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au(1)–Au(2) 3.0855(5), Au(1)–Au(3) 3.0730(6), Au(2)–Au(3) 3.0126(5), Au(1)–N 2.053(6), Au(2)–N 2.055(7), Au(3)–N 2.074(7), Au(1)–P(1) 2.253(2), Au(2)–P(2) 2.243(2), Au(3)–P(3) 2.246(2); N–Au(1)–P(1) 175.6(2), N–Au(2)–P(2) 171.7(2), N–Au(3)–P(3) 173.3(2), C(1)–N–Au(1) 119.5(5), C(1)–N–Au(2) 122.2(5), C(1)–N–Au(3) 121.5(5).

and mass spectrometric and NMR spectroscopic techniques. Single crystals of $3 \cdot 3\text{CHCl}_3$ were obtained upon layering of chloroform solutions with diethyl ether.

Through similar reactions *n*-butyl- and *n*-octylamine afforded the trinuclear complexes **4** and **5** (eq 4), which showed physical and spectroscopic properties very similar to those observed for compound **3**. Complex **5** was obtained as single crystals, $5 \cdot \text{Et}_2\text{O}$.



Crystal and Molecular Structures. Crystals of compound **5** (from dichloromethane/diethyl ether) are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units per unit cell. The lattice consists of independent tetrafluoroborate anions, *n*-octyltris[(triphenylphosphino)aurio(I)]ammonium cations, and one molecule of diethyl ether solvent. The cation has no crystallographically imposed symmetry, but the local symmetry at the quaternary nitrogen atom is close to point group C_{3v} . The *n*-octane chain is almost fully extended in the lattice, and the results of the structure determination do not suffer from disorder (Figure 1).

The geometry at the quaternary nitrogen atom resembles very closely that of previously determined structures of related compounds.¹⁵ The Au–N–Au angles are all close to or smaller than the tetrahedral standard leading to three close Au–Au contacts at the base of the NAu_3 pyramid. It is well established from experimental and theoretical results that this structural motif gives rise to significant stabilization of the system. The three gold atoms are linearly two-coordinate with standard Au–N and Au–P bond lengths and N–Au–P angles close to 180 °C.

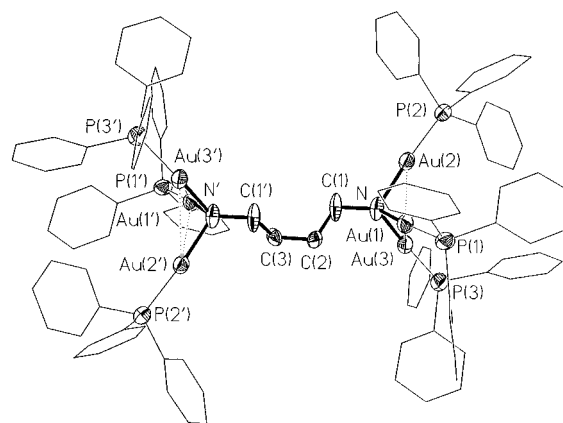


Figure 2. Molecular structure of the dication of complex **3** with atomic numbering (ORTEP, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au(1)–Au(2) 3.048(1), Au(1)–Au(3) 2.980(1), Au(2)–Au(3) 3.109(1), Au(1)–N 2.04(1), Au(2)–N 2.05(1), Au(3)–N 2.03(1), Au(1)–P(1) 2.244(4), Au(2)–P(2) 2.229(4), Au(3)–P(3) 2.233(4); N–Au(1)–P(1) 173.5(3), N–Au(2)–P(2) 175.2(3), N–Au(3)–P(3) 174.2(3), C(1)–N–Au(1) 124.2(10), C(1)–N–Au(2) 118.1(12), C(1)–N–Au(3) 119.1(11).

The overall situation at the C– NAu_3 unit is thus a good model for the anchoring of a long-chain amine in a 3-fold hollow site at the surface of gold metal.^{1,7} The bending at the carbon atom C1 leads to the tilting of the alkyl chain, which can align with neighboring units. The three phosphines are auxiliary ligands replacing the bulk of the metal in the back of the N-bonded gold atoms. The two most likely modes of thiol anchoring at gold surfaces have been discussed in ref 7.

Compound **3** also forms triclinic crystals, space group $P\bar{1}$, with $Z = 1$ formula unit in the unit cell. The lattice contains independent anions, dications, and chloroform molecules (from chloroform/diethyl ether). Crystallographically, the dications have virtual inversion symmetry owing to disorder of the two inner atoms of the butane chain (C2, C3, Figure 2). The configuration at each nitrogen atoms is the same as already described for compound **5**. The butanediamine link is thus anchored at three gold atoms on both ends in very much the same way as the *n*-octylamine chain in complex **5** on only one end.

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Supporting Information Available: Listings of crystallographic data and data collection and refinement details, atomic positional and thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (21 pages). Ordering information is given on any current masthead page.

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