J. Am. Chem. Soc. **2000,** *122,* 12598−12599

Homoleptic Gold Thiolate Catenanes

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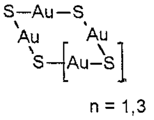
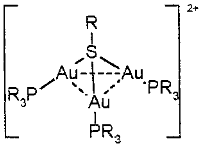
Received March 30, 2000

One of the most interesting features in the chemistry of gold is the subtle effects of weak Au···Au interactions on both the solid-state structural diversity and physical characteristics of Au(I) complexes.[1] Closed-shell attractions in these compounds are typically in the range 7−11 kcal/mol for each Au···Au bond,[2] which is of the same order of magnitude as the strength of a typical hydrogen bond. As a result both the type and extent of aggregation in many gold compounds are determined by the subtle interplay between various types of weak intermolecular interactions.[3] We recently showed[3b] that in the thiolate derivatives [Au(PPh$_3$)(SCR$_2$COOH)], association through H-bonding only (R = Me), and secondary Au···S interactions plus H-bonding (R = H), is preferred over dimerization through Au···Au attractions as found in [Au(PPh$_3$)(SCH$_3$)][4] and other phosphine-containing thiolate analogues.[5] In a search for new examples of gold compounds in which reinforcement of more than one type of weak interaction can occur, we have expanded our structural studies to include homoleptic gold thiolates. This class of molecules was chosen since the crystal structures of the three homoleptic gold thiolates which have been determined to date[6−8] all exhibit ring formation involving Au−S interactions only,[9] whereas alkanethiolate anions are capable of binding two or three [Au(PR$_3$)]$^+$ ions to afford species which contain Au···Au interactions.[4]





We now report the first two examples in gold chemistry where Au−S interactions, complemented and reinforced by multi Au···Au interactions, produce novel examples of inorganic [2]-catenanes. The only previous known examples[10] of gold catenanes are provided by its acetylide derivatives.

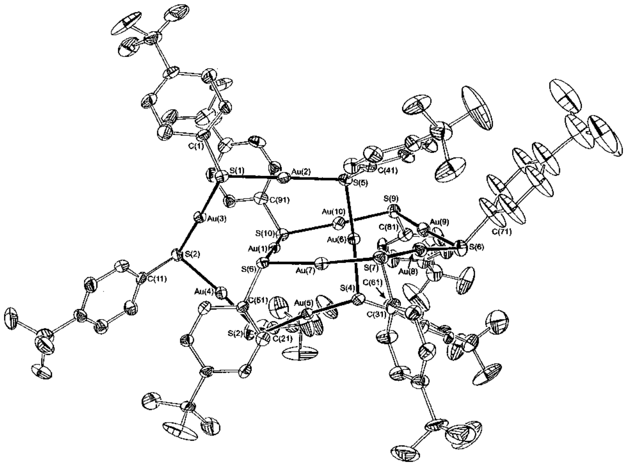


Figure 1. Thermal elipsoid plot (20% probability for clarity) of **1.** Ranges of bond lengths and angles are: Au−S, 2.289(4)−2.343(3); S−C, 1.771(8)−1.823(9) Å; Au−S−Au, 99.5(2)−107.26(14); S−Au−S, 172.52(12)−178.01(13)°.

The complexes [{Au(SC$_6$H$_4$-*p*-CMe$_3$)}$_{10}$], **1**, and [{Au(SC$_6$H$_4$-*o*-CMe$_3$)}$_{12}$], **2**, were prepared in over 90% yields by the reaction of the appropriate *tert*-butylthiophenol dissolved in xylene with an aqueous solution of [AuCl(C$_2$H$_5$SC$_2$H$_4$OH)].[11] Recrystallization of **1** from ethoxybenzene and **2** from xylene/acetonitrile yielded crystals suitable for structure determinations.[12,13] Compound **1** has been synthesized previously by a slightly different procedure,[14] but its structure was not determined. The structures of **1** and the Au$_{10}$S$_{10}$ and Au$_{12}$S$_{12}$ cores of **1** and **2** are illustrated in Figures 1−3, respectively.

The core of **1** consists of two interpenetrating pentagons defined by five S atoms and five Au atoms arranged in an alternating pattern about the periphery, with a sixth Au atom at each pentagon center. The maximum rms deviations of the central Au atoms from the least-squares planes containing gold atoms around the periphery of each pentagon are 0.068 and 0.180 Å, respectively, and the interplanar angle is 79°. The total of nine close Au···Au contacts (Table 1) which involve Au(1) and Au(6) atoms average 3.05 Å, with much longer Au···Au separations (average = 3.59 Å) occurring around the periphery of each pentagon. All four Au(1)/Au(6)−S bond lengths are 2.343(3) Å, while the remaining 16 Au−S separations lie within the narrow range 2.289(4)−2.313(4) Å. It appears that in **1** the Au−S bond lengths involving the central atoms are affected by multiple Au···Au interactions. The structure of this unique core can be readily rationalized by

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(9) Gold thiomalate, Na$_2$CsAu$_2$(L)(LH), where L = [O$_2$CCH$_2$CH(S)CO$_2$]$^{3-}$, although not strictly a homoleptic thiolate contains two interpenetrating −Au−S− helices in which the closest approach of pairs of Au atoms are 3.485(2) and 3.227(5) Å. See: Bau, R. *J. Am. Chem. Soc.* **1998**, *120*, 9380.

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(11) Complexes **1** and **2** were prepared in a two-phase reaction between aqueous [AuCl(EtSC$_2$H$_4$OH)] and the appropriate *tert*-butylthiophenol dissolved in xylene. Procedural details and analytical data are contained in the Supporting Information.

(12) Crystals of **1**·[0.8(C$_8$H$_{10}$O)] from ethoxybenzene are triclinic (*P*-1) with a = 16.641(3) Å, b = 17.274(4) Å, c = 22.703(6) Å, α = 109.45(2)°, β = 93.40(2)°, γ = 93.41(2)°, V = 6121.1(24) Å^3, D_c = 2.018 gcm^{-3}, Z = 2. Details are available in the Supporting Information.

(13) Crystals of **2** from xylene are monoclinic ($P2_1/n$), a = 18.108(2) Å, b = 26.621(6) Å, c = 30.256(4) Å, β = 99.10(3)°, V = 14401.3(41) Å^3, D_c = 2.117 gcm^{-3}, Z = 4. Details are available in the Supporting Information.

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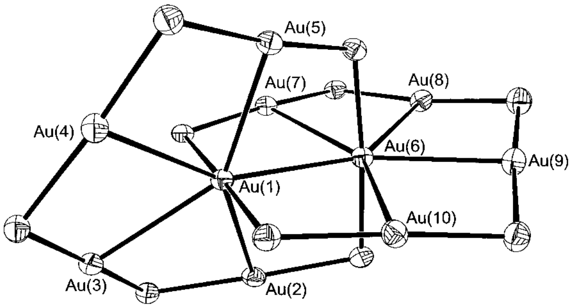


Figure 2. The $Au_{10}S_{10}$ core of **1** showing the two interpenetrating Au_5S_5 pentagons and all Au···Au interactions less than 3.15 Å.

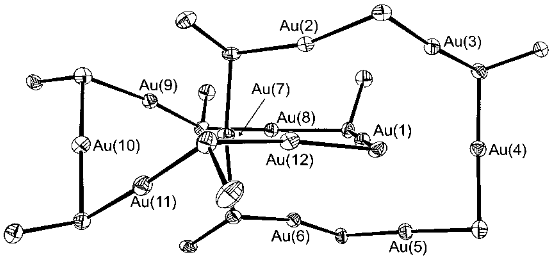
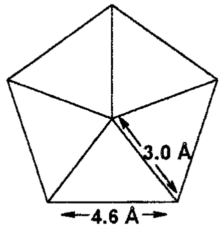


Figure 3. The $Au_{12}S_{12}$ core of **2** showing only eight alpha C atoms of the phenyl rings for clarity. Ranges of bond lengths and angles are: Au−S, 2.287(6)−2.435(5); S−C, 1.779(13)−1.819(12) Å; Au−S−Au, 88.0(2)−108.1(2); S−Au−S, 162.8(2)−178.2(2)°.

Table 1. Au···Au Separations in **1** and **2** less than 3.32 Å

compound **1**		compound **2**	
Au−Au	/Å	Au−Au	/Å
1−2	2.97	1−3	3.25
1−3	3.03	1−4	3.20
1−4	3.12	1−5	3.27
1−5	2.98	1−6	3.19
6−1	3.05	2−3	3.30
6−7	3.10	2−12	3.16
6−8	3.12	4−5	3.28
6−9	3.05	5−6	3.21
6−10	3.05	6−8	3.21
		7−8	3.22
		7−12	3.21
		10−11	3.19

consideration of the structural parameters found in many other thiolates.[15] The normal linear coordination about Au atoms combined with Au−S separations of 2.30 Å and an angular Au−S−Au arrangement averaging 105° defines a planar pentagon of side 4.6 Å. These geometric constraints maximize the number of stabilizing Au···Au contacts possible for an in-plane Au located at the center of the ring and impose a value of 3.0 Å for each Au···Au "spoke" in the pentagonal cartwheel.



The central core of **2** can also be described as a [2]catenane, but neither of the two interpenetrating hexagons, each defined by a total of 12 alternating S and Au atoms, is planar. The near linear S−Au−S arrangement with Au−S separations in the range 2.287(6)−2.325(5) (average 2.30 Å) persists in both hexagonal units, but Au···Au contacts between the central gold atoms in each ring, Au(1) and Au(7), and those on the periphery vary widely (3.19−3.69 Å), and as such are in the same range as Au···Au contacts between gold atoms around the periphery. Buckling in the second ring permits just two relatively short transannular Au···Au contacts [Au(2)···Au(12), 3.16; Au(6)···Au(8), 3.21 Å]. All Au···Au contacts less than twice the Bondi van der Waals radius of gold[16] are listed in Table 1. It is evident from packing considerations that the bulky *tert*-butyl substituent in the ortho position of the arene ring prevents the formation of a structural analogue of **1**. There are no secondary Au···S interactions of significance in either **1** or **2**.

The weakness of a single aurophilic interaction generally results in its complete disruption on dissolution, but occasionally an equilibrium is observed between associated and dissociated species.[17] The room-temperature proton NMR spectrum of **1** in noncoordinating organic solvents contains three sets of methyl and aromatic resonances in the ratio 1:2:2. This is in keeping with the inequivalence of the ligands on the periphery of interlinked pentagons as in the core of the solid. At low temperatures line broadening is followed by band splitting at −90 °C as ligand motion is restricted. We have confirmed previous findings[14] that at elevated temperatures single sets of methyl and aromatic resonances are observed, but we have been unable to determine whether the core remains intact under these conditions. Preliminary mass spectral studies using low resolution FAB revealed a complex fragmentation pattern in which $[Au_xS_y(SC_6H_4\text{-}p\text{-}CMe_3)_z)]^+$ species, $x = 5$ or 6, $y = 0−2$, $z = 5$ predominate, but which also includes higher cluster species including $[Au_{11}S_2(SC_6H_4\text{-}p\text{-}CMe_3)_9]^+$. The proton NMR spectrum of **2** is far more complex than that of **1**, and it is both temperature- and solvent-dependent, with evidence of more than one species being present in solution at ambient temperatures.

Complete dissociation of both **1** and **2** is readily effected by chemical reactions involving soft donors. Thus, in the presence of triphenylphosphine **1** forms $[Au(PPh_3)SC_6H_4\text{-}p\text{-}CMe_3]$, **3**, in almost quantitative yield. According to X-ray crystallography[18] the individual molecules have the normal quasi-linear coordination at gold with a Au−S−C bond angle of 106.6(2)°. There are no short intermolecular Au···Au or Au···S contacts present.

In summary, the electronic and structural preferences evident in many coordination complexes of Au(I) are perfectly combined in the [2]catenane structure found for the $Au_{10}S_{10}$ core of **1**. Unlike [2]catenanes which have been the subject of much recent interest[19] and are either entirely or largely organic based, there is a unique "spoke" system in both rings of **1** consisting of a total of nine Au···Au interactions which imparts structural stability.

Acknowledgment. We thank the Engineering and Physical Sciences Research Council (EPSRC) for support. We also wish to acknowledge the use of the EPSRC's National Mass Spectrometry and Chemical Database Services at Swansea and Daresbury, UK, respectively.

Supporting Information Available: Synthetic and analytical data on compounds **1** and **2**. Tables of crystallographic data including diffractometer data and refinement data, final coordinates, bond lengths, bond angles, and anisotropic displacement parameters for molecular species **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] A survey of entries in EPSRC's Chemical Database revealed an average Au−S−Au bond angle of 91° for Au(I)−thiolate derivatives containing the Au−S−Au linkage and 95° (range 105.4−82.9°) for the same angle in homoleptic Au(I)−thiolates. See The United Kingdom Chemical Database Service, Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *Chem. Inf. Comput. Sci*. **1996**, *36*, 746

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[18] Crystals of **3** from xylene/acetonitrile are triclinic (P-1), $a = 8.353(2)$ Å, $b = 11.969(3)$ Å, $c = 13.582(4)$ Å, $\alpha = 109.82(2)°$, $\beta = 103.50(2)°$, $\gamma = 93.43(2)°$, $V = 1227.7(6)$ Å^3, $D_c = 1.689$ gcm^{-3}, $Z = 2$. Full details of the structure will be published elsewhere.

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