Gold Complexes of Trithiocyanuric Acid: A Two-Dimensional Polymer Assembled through Gold(I)···Gold(I) Interactions

William J. Hunks, Michael C. Jennings, and Richard J. Puddephatt*

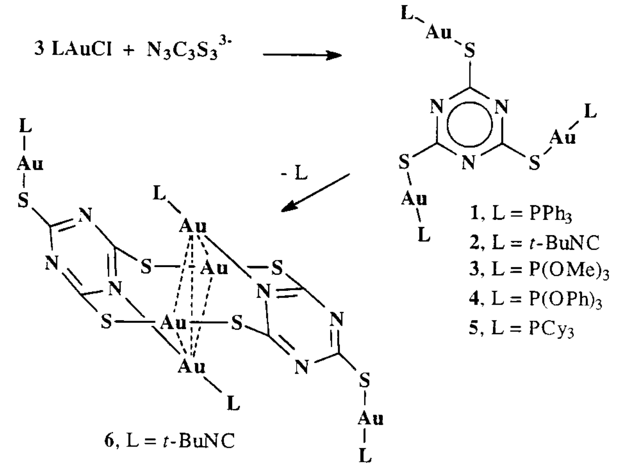
Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Received September 13, 1999

In the design of new supramolecules possessing interesting structural and physical or chemical properties, the strategy of self-assembly through weak intermolecular interactions is of central importance.[1] The mutual attraction between gold(I) centers, termed aurophilicity, is similar in strength to a hydrogen bond (7−11 kcal/mol) and so can be exploited in the design of supramolecular materials.[2−5] Short gold···gold contacts are prominent in structures of gold(I) thiolates,[2,5] most notably in the antiarthritic drug gold thiomalate which, in the derivative $Na_2CsAu_2L(LH)$ (L = $[O_2CCH_2CH(S)CO_2]^{3-}$), arranges in a double-helix structure in the solid state through −S−Au−S− chains linked by interchain Au···Au bonding.[6] These recent discoveries suggest a bright future for crystal engineering in gold(I) chemistry, and this paper reports an interesting example found in studies of trigold(I) complexes of trithiocyanuric acid, in which an unexpected reaction led to formation of an interesting sheet structure through multiple intermolecular Au···Au bonded self-assembly.[4]

Reaction of LAuCl (L = phosphine, phosphite, isocyanide) with $Na_3[(N_3C_3)S_3]$ yields the trigold complexes $[(N_3C_3)\{SAuL\}_3\text{-}2,4,6]$ (**1**−**5**) in high yield, according to Scheme 1. Complexes **1**−**5** were isolated as pale yellow air-stable solids, which were sparingly soluble in nitrobenzene/CH_2Cl_2 solutions. All complexes have been characterized by spectroscopy and by elemental analysis. They have symmetrical C_{3h} structures, as shown by the presence of singlet resonances in the ^{31}P NMR spectra of the phosphine or phosphite derivatives. The structure of complex **1** (L = PPh_3) was confirmed by X-ray diffraction and is shown in Figure 1; this structure confirms the presence of a PAuS rather than a PAuN linkage, with an approximately planar $(NCSAuP)_3$ unit. This conformation leads to short Au···N distances of 3.00−3.11 Å, shorter than the sum of the van der Waals radii for Au and N (3.25 Å). However, the P−Au−S groups are approximately linear, ranging from 175.5(2) to 177.7(2)°; therefore, any Au···N bonding must be weak.[8] In contrast, the benzene−hexathiolate complex $[\{CSAuPPh_3\}_6]$ contains 3-coordinate gold(I) centers with bridging thiolate groups.[9] As a result of the planar structure and the presence of bulky PPh_3 ligands in complex 1, there are no short intermolecular Au···Au interactions.

Scheme 1



An attempt was made to grow crystals of the derivative **2**, which has smaller *t*-BuNC ligands and so is more likely to form intermolecular Au···Au bonds. However, the complex decomposed to complex **6** during crystallization from nitrobenzene by loss of one *t*-BuNC ligand, an apparently unprecedented migration of one AuL group from sulfur to nitrogen, and dimerization, as shown in Scheme 1. Once formed, complex **6** is insoluble in common organic solvents, and it was characterized by a structure determination (Figure 2a). Complex **6** is a hexagold(I) complex and contains gold atoms in three different environments, with linear anionic $[S{-}Au(1){-}S]^-$, neutral [S−Au(2)−CN-*t*-Bu], and cationic $[N{-}Au(3){-}CN\text{-}t\text{-}Bu]^+$ units. The "dimerization" occurs by formation of two linear SAu(1)S groups by coordination to sulfur atoms from the 2,6-positions of two aromatic rings to give a 12-membered $Au_2S_4C_6$ macrocycle. An Au(3)L unit, which had

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[7] **Synthetic Procedure for $[(N_3C_3)\{SAu(PPh_3)\}_3]$ (1).** To a solution of trithiocyanuric acid trisodium salt (68 mg, 0.168 mmol) in MeOH (2 mL) was added a solution of $(Ph_3P)AuCl$ (0.250 g, 0.505 mmol) in THF (30 mL). The mixture was stirred for 12 h in the absence of light, after which the pale yellow solid precipitate was collected by filtration, washed with H_2O, MeOH, acetone, and ether, and dried under vacuum. Yield: 0.237 g, 91%. Anal. Calcd for $C_{57}H_{45}N_3S_3P_3Au_3$: C, 44.1; H, 2.9; N, 2.7. Found: C, 43.8; H, 2.9; N, 2.7. Selected data: NMR in nitrobenzene-d_5: **1**, $\delta(^{31}P)$ 36.97 (s); **2**, $\delta(^1H)$ 1.50 (s, *t*-Bu); **3**, $\delta(^1H)$ 3.86 (m, OMe), $\delta(^{31}P)$ 122.71 (s); **4**, $\delta(^{31}P)$ 105.08 (s); **5**, $\delta(^{31}P)$ 56.96 (s). IR (Nujol): **2**, $\nu(C{\equiv}N)$ 2232 cm^{-1}; **6**, $\nu(C{\equiv}N)$ 2234 cm^{-1}. X-ray data: $\mathbf{1}\cdot 2Et_2O$ (crystals grown by diffusion of ether into a solution in nitrobenzene), $C_{65}H_{65}Au_3N_3O_2P_3S_3$, fw = 1700.19, trigonal, $P\bar{3}$, $a = 29.259(1)$ Å, $c = 14.213(1)$ Å, $\gamma = 120°$, $V = 10537.4(10)$ Å^3, $Z = 6$, $d_{calcd} = 1.608$ Mg/m^3, 13 256 independent reflections, R1 = 0.0887, wR2 = 0.1584; $\mathbf{6}\cdot PhNO_2$ (crystals grown by diffusion of pentane into a solution in nitrobenzene/dichloromethane), $C_{19}H_{23}N_6S_3O_2Au_3$, fw = 1054.51, monoclinic, $P2_1/c$, $a = 11.860(2)$ Å, $b = 18.345(2)$ Å, $c = 13.176(2)$ Å, $\beta = 107.925(6)°$, $V = 2727.5(7)$ Å^3, $Z = 4$, $d_{calcd} = 2.568$ Mg/m^3, 3125 independent reflections, R1 = 0.0461, wR2 = 0.0800.

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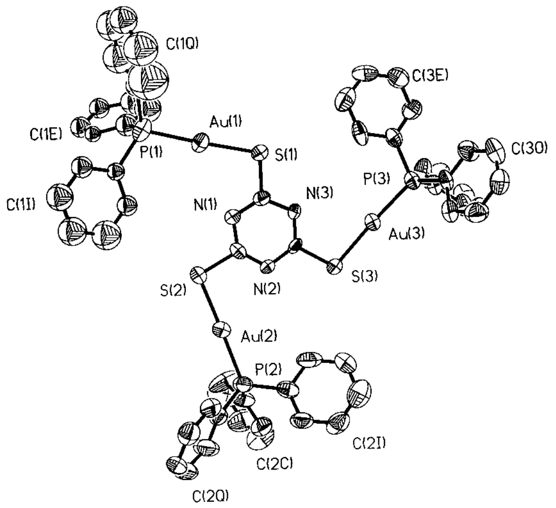

Figure 1. Molecular structure of **1** with its "manxane" core. Selected distances (Å) and angles (deg): P(1)−Au(1) = 2.262(5), S(1)−Au(1) = 2.304(4), S(3)−C(3) = 1.75(1), C(2)−N(1) = 1.34(2); P(1)−Au(1)−S(1) = 177.7(2), C(1)−S(1)−Au(1) = 101.5(6).

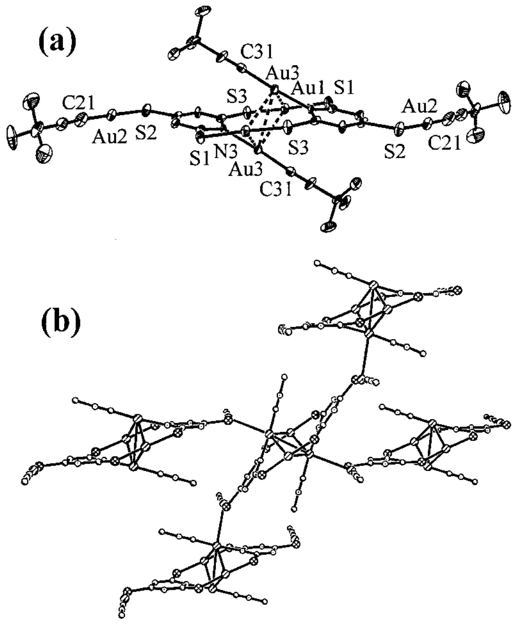

Figure 2. (a) Molecular structure of complex **6** with Au···Au bonding indicated by broken bonds. Selected distances (Å) and angles (deg): Au(1)−S(1) = 2.287(5), Au(1)−Au(3) = 2.931(1), Au(1)−Au(3)#1 = 2.941(1), Au(2)−C(21) = 1.89(3), Au(2)−S(2)#2 = 2.280(6), Au(2)−Au(3) = 3.179(1), Au(3)−C(31) = 1.96(2), Au(3)−N(3) = 2.09(1), Au(3)−Au(3)#1 = 3.240(2); S(3)#1−Au(1)−S(1) = 167.7(2), C(21)−Au(2)−S(2)#2 = 178.8(8), C(31)−Au(3)−N(3) = 175.1(7), Au(1)−Au(3)−Au(1)#1 = 113.03(3), Au(3)−Au(1)−Au(3)#1 = 66.97(3), Au(2)−Au(3)−Au(3)#1 = 167.31(4). (b) Intermolecular Au···Au bonding in **6**, showing a central molecule with its four Au···Au-bonded neighbors. Methyl substituents of the *t*-BuNC ligands are omitted for clarity.

been present in S-bonded form in **2**, is bound to the nitrogen atom in the 1-position of each aromatic ring in complex **6**. Within each molecule, the $Au(1)_2Au(3)_2$ unit forms a rhombus, with unusually short Au···Au distances of 2.931(1) and 2.941(1) Å between Au(1) and Au(3) atoms and a longer Au(3)···Au(3) contact of 3.240(2) Å, all shorter than the sum of the van der Waals radii (3.60 Å). The rhombus angles Au(1)−Au(3)−Au(1)#1 and Au(3)−Au(1)−Au(3)#1 are 113.03(3) and 66.97(3)°, respectively. The atom Au(2) is the only gold atom still present as a linear, neutral S−Au−L unit. It is attached to the sulfur atom at the 4-position of the aromatic ring (Figure 2a). The angle S−Au(1)−S = 167.7(2)° is distorted from linearity such that the gold atoms are displaced toward the center of the $Au(1)_2Au(3)_2$ rhombus, clearly indicating that the distortion results from the strong Au(1)···Au(3) aurophilic interactions; the C−Au(2)−S and C−Au(3)−N linkages in **6** are closer to being linear, at 178.8(8) and 175.1(7)°, respectively.

The nature of the rearrangement to form **6** and its molecular structure are both unusual, and the crystal structure is especially interesting. Each atom Au(2) of one molecule takes part in Au···Au bonding with the Au(3) atom of a neighboring molecule, with Au(2)··Au(3) = 3.179(1) Å, as shown in Figure 2b. Neighboring molecules are oriented orthogonal to one another to allow these Au(2)−Au(3) interactions, but all five molecules shown in Figure 2b are roughly coplanar. Overall, four of the six gold(I) centers in each molecule of **6** take part in intermolecular Au···Au bonding, and so an extended sheetlike structure is formed. The two-dimensional layers are stacked parallel, with rows of nitrobenzene molecules sandwiched between the sheets. The structure dramatically illustrates the potential for development of the Au···Au aurophilic attractions as a tool in both molecular and crystal engineering.[2−5]

Acknowledgment. We thank the NSERC of Canada for financial support.

Supporting Information Available: Tables of X-ray data and crystallographic files, in CIF format, for compounds **1** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC991085B