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Supramolecular Gold(I) Thiobarbiturate Chemistry: Combining Aurophilicity and Hydrogen Bonding to Make Polymers, Sheets, and Networks

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The cooperative forces of aurophilic and hydrogen bonding have been used in the self-assembly of phosphine or diphosphine complexes of gold(I) with the thiolate ligands derived from 2-thiobarbituric acid, $SC_4H_4N_2O_2$, by single or double deprotonation. The reaction of the corresponding gold(I) trifluoroacetate complex with $SC_4H_4N_2O_2$ gave the complexes $[Au(SC_4H_3N_2O_2)(PPh_3)]$, **1**, $[(AuSC_4H_3N_2O_2)_2(\mu\text{-LL})]$, with LL = $Ph_2PCH_2PPh_2$, **2a**, $Ph_2P(CH_2)_3PPh_2$, **2b**, or $Ph_2PCH{=}CHPPh_2$, **2c**, or the cyclic complex $[Au_2(\mu\text{-}SC_4H_2N_2O_2)(\mu\text{-}Ph_2PCH_2CH_2PPh_2)]$, **3**. In the case with LL = $Ph_2P(CH_2)_6PPh_2$, the reaction led to loss of the diphosphine ligand to give $[Au_6(SC_4H_3N_2O_2)_6]$, **4**, a hexagold(I) cluster complex in which each gold(I) center has trigonal AuS_2N coordination. Structure determinations show that **1** has no aurophilic bonding, **2b**, **3**, and **4** have intramolecular aurophilic bonding, and **2c** has intermolecular aurophilic bonding that contributes to the supramolecular structure. All the complexes undergo supramolecular association through strong NH···O and/or OH···N hydrogen bonding, and complex **3** also takes part in CH···O hydrogen bonding. The supramolecular association leads to formation of interesting polymer, sheet, or network structures, and **4** has a highly porous and stable lattice structure.

Introduction

The fields of crystal engineering and molecular recognition are current challenges in developing materials science, with one aim being the construction of metal−organic frameworks for use as functional porous solids.[1] Weak intermolecular forces, such as hydrogen bonding, π-stacking, dipole−dipole attractions, and van der Waals interactions, are used in this discipline to assemble molecular components selectively into complex structural motifs.[2] The crystalline materials may display properties distinct form those of their molecular components. The mutual attraction between gold(I) centers, called aurophilicity, has a similar strength to hydrogen bonding (7−11 kcal/mol)[3] and can be used to assemble complex supramolecular structures. The combination of aurophilic with other secondary bonding interactions, such as hydrogen bonding, has immense potential in the design of molecular materials.[4]

Polynuclear gold(I) thiolate complexes, and thiobarbiturates in particular, are of interest for several reasons. Gold(I) thiolates are often photoluminescent at room temperature, and the emission properties can be strongly affected by the presence of aurophilic Au···Au interactions, leading to potential uses as sensors.[5] The simple gold(I) thiolates have found widespread uses in gold pastes for glass and ceramics, and in self-assembled monolayers for thin-film technology or electronic devices, while derivatives of thiomalic acid or thioglucose are used in the treatment of rheumatoid arthritis.[6] There is much interest in the properties of heterocyclic thioamides, which have potential as antitumor reagents, and so many thiolatogold(I) derivatives of purines and pyrimidines have been prepared as biomimetic agents.[7] In this context, the ligand 2-thiobarbituric acid (Chart 1) has not been reported, though, having many possible tautomeric structures illustrated in Chart 1, it has very desirable properties for forming supramolecular structures.[7] The tautomers **A**−**D** (Chart 1) are expected to be in easy equilibrium, and though the thione form, **D**, is dominant in solution,[7] gold(I) derivatives are likely to be S-bonded and so derived

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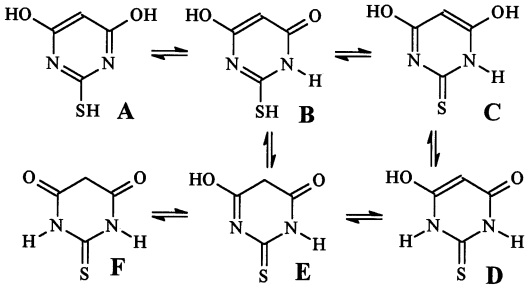
Chart 1. Some Possible Tautomers of Thiobarbituric Acid



from tautomer **A** or **B** (the tautomers **E** and **F**, having a saturated carbon atom in the ring, are not present in the free ligand as clearly indicated by the NMR spectra).[7] The tautomers **A** and **B** are ideally arranged for formation of complex supramolecular arrays through self-complementary, head-to-tail intermolecular OH···N or NH···O hydrogen bonding (equivalent in the limit of very strong hydrogen bonding) between equivalent pairs on either side of the molecule,[7] while aurophilic attractions could give additional impetus for self-assembly.[5] This paper reports the synthesis and structural characterization of complexes derived from this ligand with gold(I), using triphenylphosphine or several diphosphines as co-ligands, and shows that a particularly rich supramolecular chemistry can be obtained. Perhaps the most relevant example from the literature is the formation of a gold(I) derivative of 2-thiouracil with a monodentate phosphine co-ligand, which is known to form hydrogen bonded dimers in the solid state, but several other elegant examples are known.[4,7,8] It is also noteworthy that thiobarbituric acid has important applications in analytical chemistry and in pharmaceuticals.[7]

Results and Discussion

Synthesis and Spectra of the Complexes. Initial attempts to prepare the gold(I) complexes by the established reaction of a complex [AuClL] or $[(AuCl)_2(\mu\text{-LL})]$, L = phosphine or LL = diphosphine ligand, with the thiol 2-thiobarbituric acid in the presence of base were only partly successful. The difficulty was that the products were insoluble in common organic solvents and so were difficult to purify. Finally, pure compounds were prepared by simple reaction of the corresponding trifluoroacetate complex $[Au(O_2CCF_3)L]$ or $[(AuO_2CCF_3)_2(\mu\text{-LL})]$[9] with 2-thiobarbituric acid. The reactions occurred easily, with elimination of CF_3CO_2H, to give the products **1** or **2** as shown in Scheme 1. Still, the stable, colorless, solid products were insoluble in all common solvents except for DMSO, and so could not be recrystallized. In several cases, however, single crystals could be obtained by slow diffusion of the reagents together.

Although the reactions were carried out under the same conditions, in two cases unexpected products were formed. The reaction of $[(AuO_2CCF_3)_2(\mu\text{-LL})]$, with LL = $Ph_2P(CH_2)_2PPh_2$, led to double deprotonation of the 2-thiobarbituric acid to give the stable, colorless, cyclic complex **3**, with the bridging N,S-bonded $[C_4H_2N_2O_2S]^{2-}$ ligand, as shown in eq 1, X = CF_3CO_2. In the case with LL = $Ph_2P(CH_2)_6PPh_2$, the reaction occurred with displacement of the diphosphine ligand and single deprotonation of the 2-thiobarbituric acid to give the interesting cluster complex $[\{Au(\mu\text{-}C_4H_3N_2O_2S)\}_6]$, **4**, according to eq 2. This product **4** was also formed when

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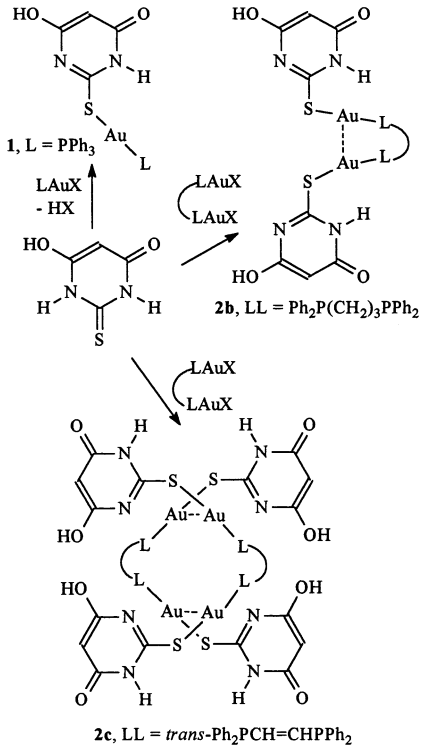
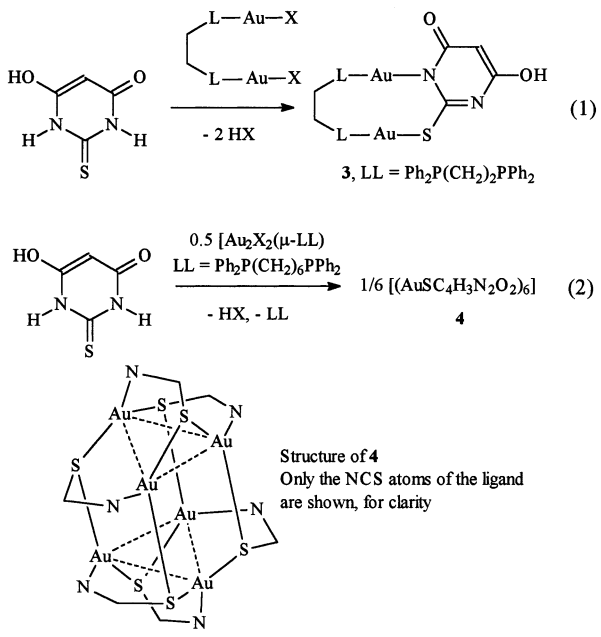
Scheme 1



LL = $Ph_2PCH_2PPh_2$ under some experimental conditions. The stable, pale yellow complex **4** was insoluble in all common solvents, and this probably accounts for the unexpected formation of the compound (phosphines are not easily displaced from gold(I) by sulfur-donor ligands). Complex **4** was characterized only by structure determination, because solution characterization was impossible.



The complexes **1**−**3** were sparingly soluble in DMSO, which is presumed to break down the intermolecular hydrogen bonding that makes the compounds insoluble in other solvents. It is, of course, possible that this solvation by DMSO could give different tautomers or even different complexes compared to the solid state structures, but the spectra were consistent with molecular structures determined crystallographically for **1**, **2b**, **2c**, and **3** and described later. For example, the ^{31}P spectra for **1** and **2** each contained a single resonance, as expected for complexes with equivalent phosphorus atoms trans to sulfur donors, whereas complex **3** gave two ^{31}P resonances for the nonequivalent phosphorus atoms trans to sulfur and nitrogen in the macrocyclic structure. No crystals suitable for structure determination were obtained for **2a**, but the observation of a single ^{31}P resonance, as well as the analytical data, supports its characterization as shown in Scheme 1, rather than as the possible structure analogous to **3**. It is not obvious why the chemistry for the diphosphine ligands is so different for varying $Ph_2P(CH_2)_nPPh_2$, giving **2** when $n = 1$ or 3, but **3** when $n = 2$. It is likely that strain in the macrocyclic structure **3** is minimized when $n = 2$, but the effect could not have been predicted. In the ^1H NMR spectra, the CH resonance of the thiolate ligand was observed in the range $\delta = 4.7-5.0$, exchange between N−H and/or O−H protons with water impurity in the solvent DMSO-d_6 occurred, and so, useful structural information was not obtained from these resonances. The tautomeric forms shown in Scheme 1 and eq 1 for the solution structures are therefore tentative.

Structures of the Complexes and the Supramolecular Association. "Molecular Tape" Structure of Complex 1. The structure of the complex [$Ph_3PAuSC_4H_3N_2O_2$], **1**, which crystallized as a tetrahydrofuran solvate, is shown in Figure 1a, with selected bond parameters in Table 1. The gold(I) center has roughly linear stereochemistry [P−Au−S = 170.67(5)°], with the distortion away from the adjacent nitrogen atom N(6). However, the orientation of the nitrogen is not suited for covalent bonding, and the distance Au···N(6) = 3.54 Å is longer than the sum of the van der Waals radii of 3.25 Å, so secondary Au···N bonding is not likely to be the cause of the distortion. The distances Au−P = 2.254(1) Å and Au−S = 2.300(1) Å are normal for linear phosphine-(thiolato)gold(I) complexes.[10] The C−S distance of 1.737(5) Å is consistent with a single bond, and the angle C(1)−S−Au = 105.1(2)° is also in the normal range for a thiolate complex.[10]

There are no intermolecular Au···Au interactions, but the molecules of complex **1** self-assemble by intermolecular hydrogen bonding as shown in Figure 1b. The pyrimidine groups associate through hydrogen bonding to give an approximately planar tape structure, with alternate phosphine-(thiolato)gold(I) groups oriented on either side and above or below the plane of the "tape". There also significant aryl−aryl interactions between phenylphosphorus groups of neighboring tapes, but these are not illustrated. The association between pyrimidine groups occurs in a head-to-tail, pairwise fashion (Figure 1b), with distances N6···O(8A) = N(6A)···O(8) = 2.71 Å and N(2)···O(7B) = N(2B)···O(7) = 2.75 Å.[11]

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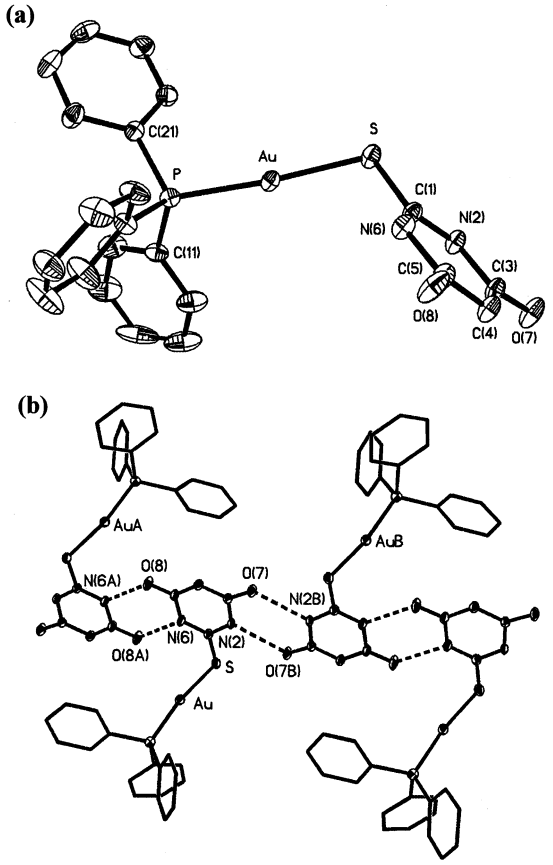

Figure 1. Structure of $[Ph_3PAuSC_4H_3N_2O_2]$, **1**: (a) molecular structure and atom labeling and (b) polymeric tape structure formed by intermolecular hydrogen bonding.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **1**

Au−P	2.254(1)	C(3)−O(7)	1.247(6)
Au−S	2.300(1)	C(5)−O(8)	1.247(6)
S−C(1)	1.737(5)	C(1)−N(6)	1.326(6)
N(6)−C(5)	1.430(6)	C(4)−C(5)	1.389(7)
C(3)−C(4)	1.395(7)	C(3)−N(2)	1.414(6)
N(2)−C(1)	1.325(6)	P−C(11)	1.800(6)
P−Au−S	170.67(5)	C(1)−S−Au	105.1(2)
C(11)−P−Au	113.1(2)	N(6)−C(1)−S	121.4(4)
C(1)−N(6)−C(5)	122.0(4)	N(6)−C(5)−O(8)	116.6(5)
N(6)−C(5)−C(4)	116.9(5)	C(5)−C(4)−C(3)	121.4(5)
C(4)−C(3)−N(2)	116.3(2)	C(3)−N(2)−C(1)	123.3(4)

The molecular structure of **1**, as described previously, suggests a gold(I) thiolate derived from either tautomeric form **A** or **B** of Chart 1. Form **A** has aromatic character whereas **B** has more localized single and double bonds. Because the hydrogen atoms were not directly located in the structure determination, the criteria are based on the degree of symmetry of the pyrimidine group. In **1**, there is no significant asymmetry from side to side. For example, the distances C(1)−N(2) = 1.325(6) Å and C(1)−N(6) = 1.326(6) Å, and C(3)−O(7) = 1.247(6) Å and C(5)−O(8) = 1.247(6) Å are effectively equal, consistent with form **A**. However, in **A**, all CN bonds should be approximately equal whereas the distances C(3)−N(2) = 1.414(6) Å and C(5)−N(6) = 1.430(6) Å are longer than the two noted previously.

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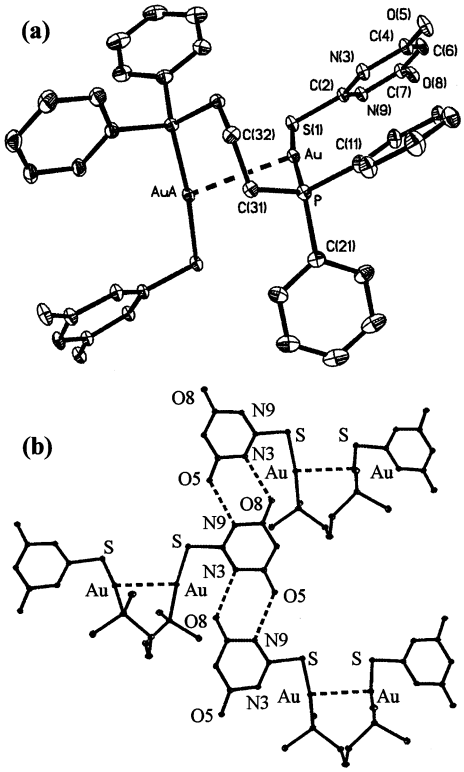


Figure 2. Structure of $[\{\mu\text{-}(CH_2)_3(PPh_2)_2\}(AuSC_4H_3N_2O_2)_2]$, **2b**: (a) structure of the digold(I) molecule with intramolecular Au···Au interaction and (b) part of the sheet structure formed by intermolecular hydrogen bonding. Only the *ipso*-carbon atoms of the phenyl groups are shown for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **2b**

Au−P	2.269(2)	Au−S(1)	2.314(2)
Au−Au(A)	3.1621(5)	C(2)−S(1)	1.740(7)
P−C(31)	1.817(7)	C(2)−N(3)	1.331(8)
C(2)−N(9)	1.323(8)	N(9)−C(7)	1.411(9)
C(7)−O(8)	1.265(8)	C(7)−C(6)	1.388(9)
C(6)−C(4)	1.383(10)	C(4)−O(5)	1.247(8)
C(4)−N(3)	1.426(9)	N(3)−C(2)	1.331(8)
P−Au−S(1)	173.94(7)	P−Au−Au(1)	84.11(5)
S(1)−Au−Au(1)	101.59(4)	C(31)−P−Au	117.2(3)
C(2)−S(1)−Au	103.5(2)	N(3)−C(2)−S(1)	122.7(5)
C(2)−N(3)−C(4)	122.1(6)	N(3)−C(4)−O(5)	116.9(6)
N(3)−C(4)−C(6)	116.7(6)	C(4)−C(6)−C(7)	121.7(7)
C(6)−C(7)−N(9)	116.4(6)	C(7)−N(9)−C(2)	123.2(6)
N(9)−C(2)−N(3)	119.7(6)	N(9)−C(7)−O(8)	115.6(6)

This observation, along with the short C−O bond distances that suggest double bond character, indicates a strong contribution from **B**. In the limit of strong hydrogen bonding, with the hydrogen atom midway between N···H···O atoms, the tautomers **A** and **B** become effectively equivalent, and this appears to be the approximate structure for complex **1** in the solid state. These conclusions apply also to complexes **2** and **4**.

Sheet Structures of Complexes 2b and 2c. The structure of complex **2b** is shown in Figure 2, and selected bond parameters are in Table 2. The complex crystallizes as **2b**·2THF·2DMF, with solvent molecules occupying cavities in the lattice. There is a 2-fold axis through the central carbon atom of the diphosphine ligand backbone, C(32), so all gold atoms are equivalent. The diphosphine adopts a twisted

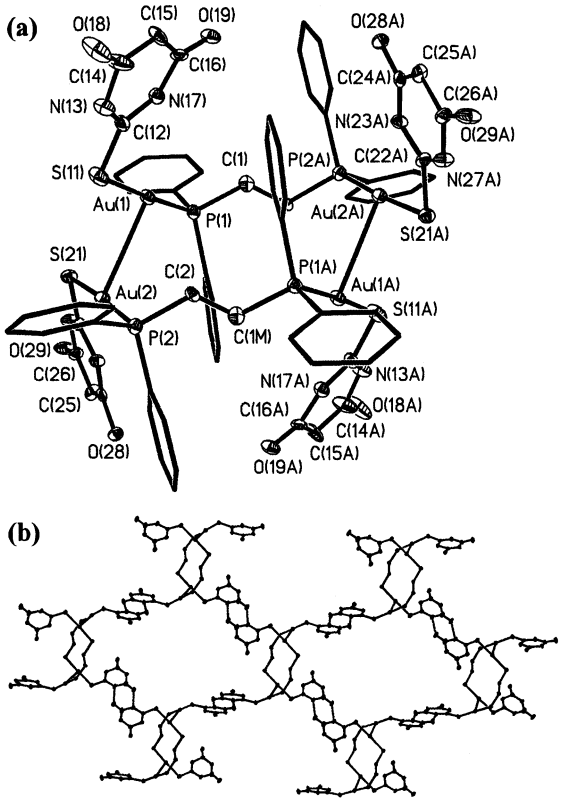


Figure 3. Structure of [(μ-*trans*-$Ph_2PCH{=}CHPPh_2$)($AuSC_4H_3N_2O_2$)$_2$], **2c**: (a) dimer of digold(I) complexes formed by intermolecular Au···Au bonding and (b) part of the sheet structure formed by a combination of hydrogen bonding and aurophilic attractions. Phenyl groups are omitted for clarity.

conformation [torsion angle AuPP(A)Au(A) = 86.6°] that allows a close intramolecular gold−gold contact with Au···Au = 3.1621(5) Å as shown in Figure 2a. Each gold(I) center has roughly linear stereochemistry with P−Au−S = 173.94(7)°, with the distortion allowing a closer gold···gold contact. The distances Au−P = 2.269(2) Å and Au−S = 2.314(2) Å are normal values.

The hydrogen bonding between individual pyrimidine units is similar to that in complex **1**, though the crystallographic symmetry is different (Figure 2b). Each pyrimidine unit is involved in four strong hydrogen bonding interactions with distances N(3)−O(8B) = N(3A)−O(8) = 2.76 Å and N(9)−O(5A) = N(9B)−O(5) = 2.66 Å, giving an extended tape structure similar to that in complex **1**. However, in **2b**, each tape is connected to a parallel one through the bridging diphosphine ligand, to give an overall sheet structure, of which only a small section is shown in Figure 2b. Because each digold(I) unit is involved in eight strong intermolecular hydrogen bonds (two pairs for each pyrimidine), it is not surprising that the network is strongly bonded together and that the compound is insoluble in most organic solvents. The Au···Au interaction in **2b** affects the conformation of the digold(I) unit but otherwise is not involved in the supramolecular association.

The structure of complex **2c** is shown in Figure 3, and selected bond parameters are listed in Table 3. The covalently bonded molecules are the expected digold(I) complexes with thiolate and bridging *trans*-bis(diphenylphosphino)ethylene

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **2c**

Au(1)−P(1)	2.264(4)	Au(1)−S(11)	2.314(4)
Au(1)−Au(2)	3.2175(9)	Au(2)−P(2)	2.252(4)
Au(2)−S(21)	2.310(4)	P(1)−C(1)	1.800(14)
S(21)−C(22)	1.74(1)	C(22)−N(23)	1.33(2)
N(23)−C(24)	1.37(2)	C(24)−O(28)	1.34(2)
C(24)−C(25)	1.34(2)	C(25)−C(26)	1.39(2)
C(26)−O(29)	1.28(2)	C(26)−N(27)	1.38(2)
N(27)−C(22)	1.32(2)	C(1)−C(2)	1.33(2)
P(1)−Au(1)−S(11)	176.9(1)	P(1)−Au(1)−Au(2)	104.7(1)
S(11)−Au(1)−Au(2)	78.3(1)	P(2)−Au(2)−S(21)	176.2(1)
P(2)−Au(2)−Au(1)	107.8(1)	S(21)−Au(2)−Au(1)	76.0(1)
C(1)−P(1)−Au(1)	108.2(5)	Au(2)−S(21)−C(22)	100.3(6)

ligands and have a U-shape as shown in Figure 3a. However, the conformation of the more rigid diphosphine ligand (P···P = 4.50 Å, Au(1)P(1)P(2A)Au(2A) = 48°] does not allow close intramolecular contact between the gold(I) centers (the intramolecular AuAu distance is 6.65 Å) of the type observed in **2b**. Instead, pairwise, intermolecular Au···Au bonding occurs to form a tetragold complex with Au(1)···Au(2) = Au(1A)···Au(2A) = 3.217(2) Å. Because there is a center of symmetry in the center of the tetragold assembly, the equivalent thiolate groups are oriented at 180° to each other. The intermolecular torsion angle, P(1)Au(1)Au(2)P(2) = 108°, is close to the ideal angle of 90° for maximizing the Au(1)···Au(2) aurophilic attraction.

Complex **2c** forms a sheet structure, but of a very different form compared to **2b**. A section of the sheet structure of **2c** is shown in Figure 3b. Each pyrimidine unit takes part in only one pairwise, intermolecular hydrogen bonding interaction with a similar unit. The heavy atoms involved are N(13)O(18) of one pyrimidine and N(27)O(29) of the other (see Figure 3a), while the other potential hydrogen bonding heavy atoms N(17)O(19) and N(23)O(28) do not participate. The relevant distances are N(13)···O(18B) = 2.73 Å and N(27)···O(29D) = 2.70 Å. The hydrogen bonding between the U-shaped dimers leads to sinusoidal chain structures, but these are cross-linked to two adjacent chains through the aurophilic attractions, and this arrangement yields an unusual sheet structure (Figure 3b). The chains are not flat, and they cross alternately above and below adjacent chains. Overall, each digold(I) unit takes part in four intermolecular hydrogen bonds and two intermolecular aurophilic attractions, giving a strongly bound supramolecular structure. The sheet structure contains large cavities that are occupied by solvate molecules, that are not shown in Figure 3b. The pyrimidine nitrogen atoms that are not involved in interdimer hydrogen bonding are oriented toward the adjacent gold atom with Au(1)N(17) = 3.37 Å and Au(2)N(23) = 3.03 Å similar to the sum of the van der Waals radii of 3.25 Å, but the gold(I) atoms are close to linear, and so, any interaction must be weak. There is a short contact N(17)···O(35A) involving an oxygen atom of a DMF solvate molecule, and this probably represents a NH···O=$CHNMe_2$ hydrogen bond. The CH group of this DMF molecule may also give a hydrogen bond to the adjacent oxygen atom of the pyrimidine, with C···O = 2.83 Å. However, the pyrimidine nitrogen atom N(23) is not involved in hydrogen bonding, and the relatively short

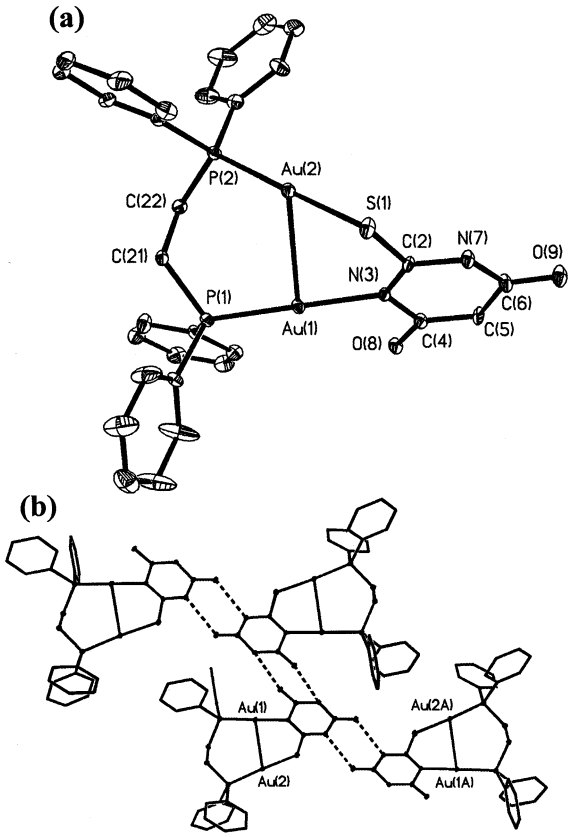


Figure 4. Structure of [{μ-$(CH_2)_2(PPh_2)_2$}Au_2{μ-$SC_4H_2N_2O_2$)], **3**: macrocyclic structure with intramolecular Au···Au bonding and (b) part of the polymeric tape structure formed by intermolecular hydrogen bonding.

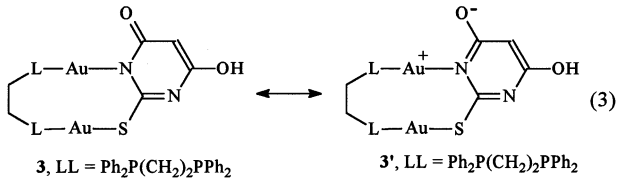
Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

Au(1)−N(3)	2.072(7)	Au(1)−P(1)	2.234(2)
Au(2)−S(1)	2.315(3)	Au(2)−P(2)	2.266(2)
Au(1)−Au(2)	2.9536(5)	C(2)−S(1)	1.743(9)
N(3)−C(4)	1.42(1)	N(3)−C(2)	1.32(1)
C(4)−C(5)	1.38(1)	C(5)−C(6)	1.42(1)
C(6)−O(9)	1.25(1)	C(6)−N(7)	1.36(1)
N(7)−C(2)	1.35(1)	C(4)−O(8)	1.27(1)
N(3)−Au(1)−P(1)	179.2(2)	N(3)−Au(1)−Au(2)	83.8(2)
P(1)−Au(1)−Au(2)	96.94(6)	P(2)−Au(2)−S(1)	176.18(8)
P(2)−Au(2)−Au(1)	103.37(6)	S(1)−Au(2)−Au(1)	80.14(6)
C(2)−S(1)−Au(2)	104.3(3)	S(1)−C(2)−N(3)	123.4(6)
C(2)−N(3)−Au(1)	123.2(6)	C(2)−N(3)−C(4)	117.7(7)

distance Au(2)N(23) = 3.03 Å may be indicative of a weak gold−nitrogen secondary bond.

Structure of the Cyclic Compound 3. The molecular structure of [Au_2(μ-$SC_4H_2N_2O_2$)(μ-$Ph_2P(CH_2)_2PPh_2$)], **3**, is shown in Figure 4, and selected bond distances and angles are listed in Table 4. The complex exists as a macrocycle with the two gold(I) centers having PAuS and PAuN coordination, and with intramolecular Au···Au bonding [Au···Au = 2.9536(5) Å].[12] The doubly deprotonated thiobarbituric acid ligand bridges the two metal centers through its sulfur and nitrogen donor atoms. The distances Au−N = 2.072(7) Å and Au−S = 2.315(3) Å are unexceptional, while the distance P−Au = 2.234(2) Å trans to N is slightly shorter than P−Au = 2.266(2) Å trans to S. The angles P−Au−N = 179.2(2)° and P−Au−S = 176.18(8)° are approximately linear. Examples of N,S-coordination to two gold(I) centers by other N-heterocyclic thiolates are known,[7,13] and exchange between N- and S-coordinated gold(I) centers has been reported.[7,14] The nine-membered macrocycle in **3** is twisted, with the angle C(2)S(1)Au(2) = 104.3(3)° and torsion angle P−Au−Au−P = 34.5°.

Because the thiolate ligand in **3** is doubly deprotonated, $[C_4H_2N_2O_2S]^{2-}$, only one pairwise N···H···O hydrogen bonding unit is possible, and this occurs to give "dimer of digold" units [Figure 3b, N(7)···O(9A) = N(7A)···O(9) = 2.737 Å]. However, a second pairwise hydrogen bonding interaction of the type C−H···O is also formed [Figure 3b, C(5)···O(8A) = C(5A)···O(8) = 3.181 Å], and although such CH···O hydrogen bonds are usually weak, this one is toward the short end of the range for such bonds of 3−4 Å.[15] The presence of this CH···O hydrogen bond, along with the pattern of bond distances in the thiobarbiturate ring, suggests a strong component of the resonance form **3′** having an anionic oxygen center (eq 3).



3, LL = $Ph_2P(CH_2)_2PPh_2$ **3'**, LL = $Ph_2P(CH_2)_2PPh_2$

The two pairwise H-bonding interactions lead to the self-assembly to give a one-dimensional tape structure, with digold(I) units alternating on either side as shown in Figure 3b. The tapes are arranged side by side and stack above one another through phenyl···phenyl interactions, with solvent molecules filling the voids.

Network Structure of Complex 4. The structure of the hexagold cluster, [{$AuSC_4H_3N_2O_2$}$_6$], **4**, is shown in Figure 5, with selected bond parameters in Table 5. The complex crystallized in the approximate formula **4**·11DMF·$6H_2O$. There was considerable disorder of some of the many solvate molecules that was only partly resolved, leading to poor agreement factors, but the important structural features are clear. The six gold atoms adopt a trigonal antiprismatic arrangement with inversion symmetry relating the two halves. Each gold(I) center is trigonally coordinated to a pyrimidine nitrogen [Au−N = 2.25(2)−2.29(2) Å] and by two bridging sulfur atoms [Au−S = 2.451(6)−2.522(7) Å].[16] Furthermore, each gold atom exhibits secondary Au···Au bonding to two other gold atoms forming a triangle [Au(1)Au(2) = 3.062(3) Å, Au(1)Au(3) = 2.960(3) Å, Au(2)Au(3) = 3.103(3) Å], indicated by broken lines in Figure 5a. The other gold···gold distances [Au(1)Au(2A) = 3.617 Å, Au(1)Au(3A) = 3.746 Å, Au(2)Au(3A) = 3.512 Å] are about equal to the sum of

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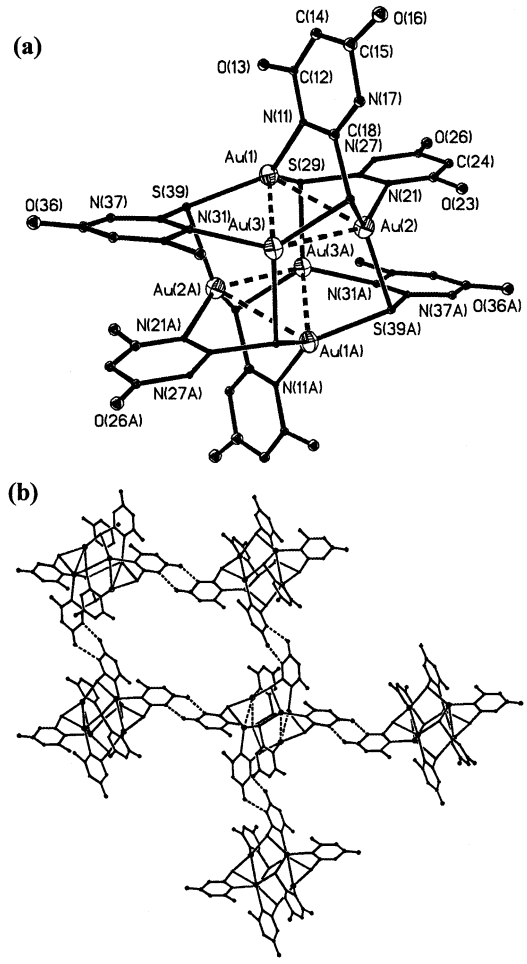

Figure 5. Structure of $[Au_6(\mu\text{-}SC_4H_3N_2O_2)_6]$, **4**: (a) hexagold(I) cluster complex and (b) cross section of the distorted face-centered cubic lattice formed by intermolecular hydrogen bonding.

Table 5. Bond Lengths [Å] and Angles [deg] for Complex **4**

Au(1)−Au(2)	3.062(3)	Au(1)−Au(3)	2.960(3)
Au(2)−Au(3)	3.103(3)	Au(1)−N(11)	2.25(2)
Au(1)−S(39)	2.487(6)	Au(1)−S(29)	2.487(6)
Au(2)−N(21)	2.29(2)	Au(2)−S(19)	2.458(7)
Au(2)−S(39A)	2.499(7)	Au(3)−N(31)	2.28(2)
Au(3)−S(19)	2.451(6)	Au(3)−S(29A)	2.522(7)
N(11)−Au(1)−S(39)	130.4(5)	N(11)−Au(1)−S(29)	120.4(5)
S(39)−Au(1)−S(29)	105.6(2)	N(21)−Au(2)−S(19)	127.2(5)
N(21)−Au(2)−S(39)	103.6(5)	S(19)−Au(2)−S(39)	123.5(2)
N(31)−Au(3)−S(19)	130.6(5)	N(31)−Au(3)−S(29A)	104.7(5)
S(19)−Au(3)−S(29A)	120.9(2)	Au(3)−S(19)−Au(2)	78.4(2)
Au(1)−S(29)−Au(3)	96.8(2)	Au(1)−S(39)−Au(2A)	93.0(2)

the van der Waals radii (3.6 Å) and are not shown as secondary bonds in **4**, though there could still be weak attractions at such distances. Only one unique gold···gold bonded edge of the hexagold unit is bridged by a sulfur atom, and it naturally gives a smaller angle at sulfur [Au(2)S(19)Au(3) = 78.4(2)°] than the angles at sulfur bridging between gold atoms with no aurophilic attraction [Au(1)S(29)Au(3A) = 96.8(2)°, Au(1)S(39)Au(2A) = 93.0(2)°]. The cluster stereochemistry also leads to considerable distortions from trigonal stereochemistry at gold(I), with angles NAuS = 103.6(5)−130.6(5)° and SAuS = 105.6(2)−123.5(2)° (Table 5).

Hydrogen bonding (N−H···O) assembles these aggregates into a distorted face-centered cubic lattice, as illustrated in Figure 5b, which shows a central hexagold(I) unit, surrounded by only four of its six nearest neighbors, and just one face of one of the resulting "cubes". Each ligand takes part in only one pairwise hydrogen bonding interaction (Figure 5b), with one ligand binding to its crystallographically equivalent group [O(16)···N(17B) = O(16B)..N(17) = 2.65 Å] and two to nonequivalent ligands [O(26)···N(37D) = O(36D)···N(27) = O(36)···N(27F) = O(26F)···N(37) = 2.79 Å]. There are large channels in the structure (cross-channel distances of 10−15 Å), which contain the dimethylformamide and water solvate molecules. The free hydroxyl groups (those not involved in the intermolecular association between hexagold clusters) are each hydrogen bonded to a water molecule [O(13)···O(101) = 2.51 Å, O(23)···(O41) = 2.56 Å, O(33)···O(100) = 2.60 Å]. Bridging sulfur atoms have been used before in the formation of multinuclear gold aggregates,[17] but this highly porous and very stable structure **4** (Figure 5b) is particularly interesting in providing a lattice structure reminiscent of a zeolite but held together by coordinate bonds, hydrogen bonds, and aurophilic attractions.

Conclusions

This work shows clearly how the combination of coordination chemistry, aurophilic interactions, and hydrogen bonding can give a very rich chemistry of gold(I) with ligands derived from deprotonated thiobarbituric acid. Several complexes of the mono-deprotonated ligand and one complex of the bis-deprotonated ligand were obtained in crystalline form. The thiolate complex with triphenylphosphine forms a tape structure while, with the diphosphine co-ligands, two very different sheet structures are formed, and with no co-ligands, a roughly face-centered cubic network of hexagold clusters is formed. Double deprotonation of the thiobarbituric acid leads to formation of a macrocyclic complex, and it too undergoes intermolecular hydrogen bonding to give a different type of polymeric tape structure. Clearly, the system studied here of gold(I) with phosphines and thiobarbituric acid demonstrates the value of combining aurophilic and hydrogen bonding in the construction of supramolecular entities by self-assembly. The photoluminescent properties of gold thiolates suggest promise in the synthesis of functional materials, and preliminary study of these compounds shows that they give strong emission at room temperature (see Experimental Section).

Experimental Section

The reagents $[AuCl(SMe_2)]$, and $[(CH_2)_n(Ph_2PAuCl)_2]$ were prepared as previously described.[9] NMR spectra were recorded by using a Varian Mercury 400 MHz spectrometer, with ^1H NMR chemical shifts reported relative to TMS and ^{31}P chemical shifts reported relative to an 85% H_3PO_4 external standard. The complexes were only slightly soluble in DMSO-d_6, and the N−H and O−H protons underwent rapid exchange with protons of impurity water in the solvent. IR spectra were recorded as Nujol mulls by using a

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Table 6. Crystallographic Data for Complexes **1**, **2a**, **2b**, **3**, **4**

	1·THF	**2b**·2THF·2DMF	**2c**·3DMF·MeOH	**3**·2.5THF·0.5DMF	**4**·11DMF·6H_2O
formula	$C_{26}H_{22}AuN_2O_3PS$	$C_{49}H_{54}Au_2N_6O_8P_2S_2$	$C_{43.75}H_{52}Au_2N_7O_{7.75}P_2S_2$	$C_{41.5}H_{39}Au_2N_{2.50}O_5P_2S$	$C_{57}H_{82}Au_6N_{23}O_{29}S_6$
fw	640.45	1374.97	1319.92	1140.69	2927.61
T/K	294(2)	150(2) K	200(2)	200(2)	200(2)
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	triclinic	triclinic	monoclinic
space group	*P*2(1)/*n*	*Pbcn*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*
cell dimens: *a*/Å	8.9262(1)	19.5868(6)	14.262(2)	9.0232(3)	31.150(4)
b/Å	27.9619(3)	11.8261(3)	14.799(2)	11.7995(9)	22.367(3)
c/Å	11.0625(2)	22.2825(6)	15.027(3)	21.6567(9)	14.469(2)
α/deg	90	90	60.664(7)	83.222(2)	90
β/deg	108.679(1)	90	65.330(7)	79.145(2)	111.407(7)
γ/deg	90	90	69.976(7)	85.193(2)	90
V/Å^3	2615.69(6)	5161.4(2)	2474.1(7)	2244.2(2)	9386(2)
Z	4	4	2	2	4
d(calcd)/Mg/m^3	1.703	1.769	1.772	1.688	2.072
abs coeff/mm^{-1}	5.794	5.879	6.128	6.690	9.559
F(000)	1304	2696	1291	1099	5548
cryst size/mm^3	0.10 × 0.08 × 0.02	0.60 × 0.21 × 0.18	0.15 × 0.10 × 0.03	0.43 × 0.24 × 0.07	0.10 × 0.08 × 0.03
indep reflns	4547[R(int) = 0.070]	5909[*R*(int) = 0.076]	9378[*R*(int) = 0.073]	12823[*R*(int) = 0.059]	5324[*R*(int) = 0.130]
abs corr	integration	integration	integration	integration	integration
data/restraints/params	4547/0/282	5909/4/290	9378/24/456	12823/34/388	5324/3/262
GOF on F^2	0.961	0.977	0.912	0.997	1.264
R1 [$I > 2\sigma(I)$]	0.0354,	0.0490	0.0753	0.0697	0.1109
wR2 [$I > 2\sigma(I)$]	0.0673	0.1431	0.1415	0.1893	0.3342

Perkin-Elmer 2000 FTIR. Emission spectra were recorded at room temperature by using a Fluorolog-3 spectrofluorometer using a 3 nm slit width and with excitation at λ = 350 nm. Many of the intermediate gold(I)−trifluoroacetate complexes are light sensitive and should be handled with minimum light exposure.

[$Ph_3PAuSC_4H_3N_2O_2$], 1. Silver trifluoracetate (0.163 g, 0.707 mmol) in MeOH (2 mL) was added to a solution of [Ph_3PAuCl] (0.350 g, 0.707 mmol) in THF (10 mL). The mixture was stirred for 30 min and then filtered through Celite. A solution of thiobarbituric acid (0.102 g, 0.707 mmol) in DMF (5 mL) was added. The mixture was stirred for 1 h, and the resulting colorless solid was collected by filtration, and washed with DMF, CH_2Cl_2, acetone, and ether. Yield: 0.392 g (92%). NMR (d_6-DMSO): $\delta(^1H)$ = 7.62−7.60 [m, 15H, PPh_3], 4.94 [s, 1H, ArH]; $\delta(^{31}P)$ = 38.18 [s]. IR (Nujol): ν(C═O) = 1677, 1652, 1604 cm^{-1}; ν(NH···O) = 2611 cm^{-1} (br). Anal. Calcd for $C_{22}H_{18}N_2O_2PSAu$: C, 43.9; H, 3.0; N, 4.6. Found: C, 44.2; H, 3.4; N, 4.9%. λ_{em} = 450 nm. Crystals of **1**·THF were grown from a solution of DMF, THF, and MeOH as colorless needles.

[{μ-$CH_2(PPh_2)_2$}($AuSC_4H_3N_2O_2$)$_2$], 2a. This compound was prepared similarly to **1**, from [{μ-$CH_2(PPh_2)_2$}$(AuCl)_2$]. Yield: 74%. NMR (d_6-DMSO): $\delta(^1H)$ = 7.78−7.37 [m, 20H, PPh_2], 4.73 [s, 2H, ArH], 3.42 [m, 2H, dppm]; $\delta(^{31}P)$ = 32.40 [s]. IR (Nujol): ν(C═O) = 1645, 1608 cm^{-1}; ν(NH···O) = 2710 cm^{-1} (br). Anal. Calcd for $C_{33}H_{28}N_4O_4P_2S_2Au_2$: C, 37.2; H, 2.6; N, 5.3. Found: C, 37.1; H, 2.7; N, 5.3%. λ_{em} = 478 nm.

[{μ-$(CH_2)_3(PPh_2)_2$}($AuSC_4H_3N_2O_2$)$_2$], 2b. This compound was prepared similarly to **1**, from [{μ-$(CH_2)_3(PPh_2)_2$}$(AuCl)_2$]. Yield: 84%. NMR (d_6-DMSO): $\delta(^1H)$ = 7.83−7.51 [m, 20H, PPh_2], 4.94 [s, 2H, ArH], 2.99 [m, 4H, dppp], 1.85 [m, 2H, dppp]; $\delta(^{31}P)$ = 31.60 [s]. IR (Nujol): ν(C═O) = 1648, 1612 cm^{-1}; ν(NH···O) = 2700 cm^{-1} (br). Anal. Calcd for $C_{35}H_{32}N_4O_4P_2S_2Au_2$: C, 38.5; H, 2.9; N, 5.1. Found: C, 37.9; H, 2.8; N, 5.4%. λ_{em} = 468 nm. Crystals of **2b**·2THF ·2DMF were grown from a solution of THF, DMF, and methanol as orange plates.

[(*trans*-1,2-Ph_2PCH═$CHPPh_2$)($AuSC_4H_3N_2O_2$)$_2$], 2c. This compound was prepared similarly to **1**, from [(*trans*-1,2-Ph_2PCH═$CHPPh_2$)$(AuCl)_2$]. Yield: 64%. NMR (d_6-DMSO): $\delta(^1H)$ = 7.80−7.57 [m, 20H, PPh_2], 7.70 [br, 2H, CH═CH], 4.93 [s, 2H, ArH]; $\delta(^{31}P)$ = 35.00 [s]. IR (Nujol): ν(C═O) = 1640, 1597 cm^{-1}; ν(NH···O) = 2607 cm^{-1} (br). Anal. Calcd for $C_{34}H_{28}N_4O_4P_2S_2Au_2$: C, 37.9; H, 2.6; N, 5.2. Found: C, 37.8; H, 2.6; N, 5.2%. λ_{em} = 457 nm. Crystals of **2c**·6DMF·1.5MeOH were grown from a solution of THF, DMF, and methanol as colorless plates.

[{μ-$(CH_2)_2(PPh_2)_2$}Au_2(μ-$SC_4H_2N_2O_2$], 3. Prepared similarly to **1**, from [{μ-$(CH_2)_2(PPh_2)_2$}$(AuCl)_2$]. Yield: 77%. NMR (d_6-DMSO): $\delta(^1H)$ = 7.87−7.52 [m, 20H, PPh_2], 5.18 [s, 1H, ArH], 2.97, 3.00 [m, 4H, PCH_2(a)CH_2(b)P]; $\delta(^{31}P)$ = 36.67 [s, P−Au−S], 28.97 [s, P−Au−N]. IR (Nujol): ν(C═O) = 1640, 1617 cm^{-1}, ν(NH···O) = 2680 cm^{-1} (br). Anal. Calcd for $C_{30}H_{26}Au_2N_2O_2P_2S$·$2H_2O$: C, 37.1; H, 3.1; N, 2.9. Found: C, 36.8; H, 2.5; N, 2.7%. λ_{em} = 467 nm. Crystals of [{μ-dppe}Au_2{μ-$SC_4N_2O_2H_2$}]·2.5THF·0.5DMF were grown as colorless, rectangular plates from a solution of THF, DMF, and methanol.

[($Au(SC_4H_3N_2O_2)_6$], 4. Crystals of [Au_6(μ_3-$SC_4H_3N_2O_2H_2)_6$]·11DMF·$6H_2O$ were grown by layering a solution of thiobarbituric acid in DMF with [(μ-$(CH_2)(PPh_2)_2$}$(AuO_2CCF_3)_2$] in THF/MeOH forming yellow, rectangular plates. The small crystal diffracted weakly and easily lost some of the occluded solvent. The compound was insoluble in all common organic solvents. Anal. Calcd for $C_{24}H_{18}N_{12}O_{12}S_6Au_6$·8DMF: C, 22.0; H, 2.8; N, 10.7. Found: C, 22.1; H, 2.4; N, 11.4%.

X-ray Structure Determinations. Crystals were mounted on glass fibers, and data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and structure solution and refinement were carried out using the SHELXTL 5.1 (Sheldrick, G. M., Madison, WI) program package. The hydrogen atoms were not located directly but were riding on their respective C, N, or O atoms. The crystal data and refinement parameters are listed in Table 6.

Complex 1·THF. The heavy atoms were refined anisotropically, except for those of the solvate THF molecule, which were modeled isotropically. The largest residual electron density peak (0.826 e/Å^3) was associated with the gold atom.

Complex 2b·2THF·2DMF. There was an axis of symmetry through the center of each molecule of **2b**. All non-hydrogen atoms of **2b** were refined anisotropically. Hydrogen atoms involved in

H-bonding were modeled as four-half-occupancy atoms, riding on each of the oxygen and nitrogen atoms. The atoms of the THF and DMF solvate molecules were modeled isotropically, and some bond lengths of the disordered DMF were fixed [CO = 1.21 Å, CN = 1.31 Å, N−Me = 1.45 Å]. The largest residual electron density peak (2.433 e/Å^3) was associated with a disordered solvent molecule.

Complex (2c)$_2$·6DMF·1.5MeOH. There was a center of symmetry at the center of the dimer. The hydrogen atoms involved in intermolecular H-bonding were riding on the N-atom while, for the NCOH groups not involved in such bonding, the H atom was riding on the O-atom. The solvent molecules were modeled isotropically, and hydrogen atoms were included. Some of the DMF molecules were disordered and were treated as rigid groups. The methanol molecules were modeled at 75% occupancy. The largest residual electron density peak (1.936 e/Å^3) was associated with one of the gold atoms.

Complex 3·2.5THF·0.5DMF. All the non-hydrogen atoms of **3** were refined anisotropically. The THF molecules of solvation were modeled isotropically with hydrogen atoms included, and with some geometrical constraints. The DMF was modeled isotropically at 0.5 occupancy and with constrained bond distances. The largest residual electron density peak (5.265 e/Å^3) was associated with one of the gold atoms.

Complex 4·11DMF·6H$_2$O. There was a center of symmetry at the center of the hexagold cluster complex. The small, highly insoluble crystal diffracted weakly, and the lattice contained many solvate molecules, some of which were disordered. The residuals were therefore high. Only the gold atoms were refined anisotropically. Five of the DMF molecules were refined isotropically with hydrogen atoms included. The remaining DMF molecule was straddling a 2-fold axis, and was poorly resolved, so H-atoms were not included, and the bond lengths were fixed. The water molecules were modeled as isotropic oxygen atoms, and H-atoms were not included. The largest residual electron density peak (3.066 e/Å^3) was associated with one of the sulfur atoms.

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Supporting Information Available: Tables of X-ray data for complexes **1**, **2b**, **2c**, **3**, **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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