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$\{[\mathrm{AuL}_2]^+[\mathrm{LAuCl}][\mathrm{AuCl}_2]^-\}$ (L = 2-Aminopyridine): A Trinuclear Gold(I) Unit in the Pattern [+ Neutral −]

John H. K. Yip,* Ren Feng, and Jagadese J. Vittal

Department of Chemistry, The National University of Singapore, 10 Kent Ridge Crescent, Singapore, 119260

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Many linear two coordinate gold(I) complexes are known to form supramolecular assemblies in solid state, primarily due to a sub van der Waals attraction between closed-shell Au(I) ions.[1] The Au(I)···Au(I) attraction, christened "aurophilicity" by Schmidbaur, was found to have a bond energy similar to that of the hydrogen bond (6−11 kcal/mol).[2] Apart from aurophilicity, other weak interactions such as the Coulombic force also play a role in determining the solid state arrangement of Au(I) complexes. Of particular interest are the ionic complexes $\{[\mathrm{AuL}'_2]^+[\mathrm{AuX}_2]^-\}$ (L′ = neutral ligand, X = anionic ligands). Being composed of both cationic and anionic Au(I) species, the compounds $\{[\mathrm{AuL}'_2]^+[\mathrm{AuX}_2]^-\}$ offer opportunities for examining how the interplay of aurophilicity and electrostatic interaction controls the solid-state aggregation of ionic Au(I) species. For many ionic gold(I) compounds such as $\{[\mathrm{Au(tetrahydrothiophene)}_2]^+[\mathrm{AuI}_2]^-\}_n$,[3] $\{[\mathrm{Au(pyridine)}_2]^+[\mathrm{AuBr}_2]^-\}_n$,[4] and $\{[\mathrm{Au(3\text{-}picoline)}_2]^+[\mathrm{AuCl}_2]^-\}_n$,[5] cations (+) and anions (−) are arranged alternatively in the solid state, forming a pattern [+ − + −]. The alternate arrangement of the oppositely charged Au(I) ions is favorable because it allows the electrostatic interaction to be optimized. However, there are two notable exceptions to the prevailing pattern [+ − + −]: the tetrameric $\{[\mathrm{Au(pyridine)}_2]^+[\mathrm{AuX}'_2]^-\}_2$ (X' = Cl, Br, I)[4,6] and $\{[\mathrm{Au(PPhMe}_2)]^+[\mathrm{Au(GeCl}_3)_2]^-\}_2$[7] are found to display patterns [− + + −] and [+ − − +], respectively. In contrast to simple considerations of Coulombic repulsion, two cations/anions are juxtaposed in these patterns. The Au···Au distance between the two anions $[\mathrm{Au(GeCl}_3)_2]^-$ in the compound $\{[\mathrm{Au(PPhMe}_2]^+[\mathrm{Au(GeCl}_3)_2]^-\}_2$ is exceptionally short (2.881(1) Å),[7] indicating the presence of relatively strong aurophilic attraction between the two Au atoms. The strong aurophilic interaction overrules the Coulombic repulsion between the two Au(I) ions, leading to the unusual pattern [+ − − +]. Besides, aurophilicity has been shown to be responsible for the dimerization of two cationic $[\mathrm{Au}_2(\mu\text{-SCH}_2\mathrm{Ph})(\mathrm{PPh}_3)_2]^+$ complexes in the solid state.[8]

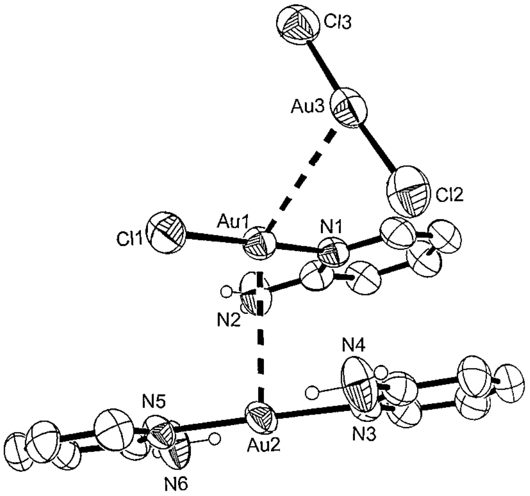

Figure 1. Diagram showing the molecular structure of the compound $\{[\mathrm{AuL}_2]^+[\mathrm{LAuCl}][\mathrm{AuCl}_2]^-\}$, **1** (ORTEP, 50% probability ellipsoids, aromatic hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Au(1)−N(1), 2.053(5); Au(1)−Cl(1), 2.2631(9); Au(2)−N(3), 2.025(5); Au(2)−N(5), 2.019(5); Au(3)−Cl(2), 2.259(2); Au(3)−Cl(3), 2.261(2); Au(1)−Au(2), 3.3335(3); Au(1)−Au(3), 3.2729(4); N(1)−Au(1)−Cl(1), 176.11(15); N(5)−Au(2)−N(3), 179.0(2); Cl(2)−Au(3)−Cl(3), 175.88(8); Cl(1)−Au(1)−Au(2)−N(5), 46.04(0.17); Cl(1)−Au(1)−Au(3)−Cl(2), 91.58(0.07).

Au(I) complexes with nitrogen donor ligands have received relatively little attention, compared to the complexes which contain phosphorus donor ligands.[9] This is partly due to the instability of the complexes formed from the "soft" Au(I) ion and the "hard" nitrogen donor ligands. Nevertheless, several recent studies have highlighted the important role played by weak intermolecular interactions such as the intermolecular N−H···O/Cl/Br hydrogen bond in stabilizing some Au(I)-amine or -ketimine complexes.[10] In this study we investigated the structural chemistry of Au(I) complexes which contain 2-aminopyridine (L) as the ligand. The nitrogen atom in the pyridine ring is expected to coordinate to the soft gold(I) ion whereas the dangling NH$_2$-group can form hydrogen bonds with acceptor groups such as chloride (N−H···Cl). We found that the reaction between $[\mathrm{Au(SMe}_2)\mathrm{Cl}]$ and 2-aminopyridine led to the formation of a trimeric compound $\{[\mathrm{AuL}_2]^+[\mathrm{LAuCl}][\mathrm{AuCl}_2]^-\}$ (L = 2-aminopyridine), **1**, shown in Figure 1. Surprisingly, X-ray analysis showed that a single crystal of **1** is composed of cation $[\mathrm{AuL}_2]^+$, anion $[\mathrm{AuCl}_2]^-$, and neutral complex [LAuCl] in the ratio 1:1:1. Furthermore, the three Au(I) complexes are arranged in a novel pattern [+ neutral −]. Additionally, the Au(I) complexes aggregate to form two-dimensional networks in solid state, *via* cooperative action of aurophilic interactions and N−H···Cl hydrogen bonds.

Experimental Section

General Method. The KAuCl_4 was purchased from Oxkem and the 2-aminopyridne and dimethyl sulfide were obtained from Aldrich and were used without further purification. $[\mathrm{Au(SMe}_2)\mathrm{Cl}]$ was synthesized

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* To whom correspondence should be addressed. Tel.: +65-874-6256. Fax: +65-779-1691. E-mail: chmyiphk@nus.edu.sg.

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Table 1. Crystal Data for 1

formula	$C_{15}H_{18}Au_3Cl_3N_6$
cryst syst	monoclinic
space group	$P2(1)/n$
lattice params	$a = 10.5972(1)$ Å, $b = 11.6988(1)$ Å and $c = 17.9547(1)$ Å
V (Å^3)	2128.83(3)
Z	4
density (calc) (g/cm^3)	3.056
abs coeff	21.013 mm^{-1}
radiation	0.710 73 Å
F(000)	1752
temp (K)	293(2)
no. of unique reflns	5305
no. of params varied	245
final R indices[a]	R1 = 0.0318, wR2 = 0.0748
goodness of fit (GOF)	1.050

[a] $R1 = (||F_o| - |F_c||)/(|F_o|)$; $wR2 = [(w(F_o^2 - F_c^2)/(wF_o^4]^{1/2}$; GOF $= [(w(F_o^2 \text{ to } F_c^2)^2/(n-p)]^{1/2}$ where n is the number of reflections and p is the number of parameters refined.

according to the reported method.[11] The room temperature and 77 K luminescent properties of compound **1** were checked on a Perkin-Elmer LS 50B fluorescence spectrophotometer.

Preparation of {$[AuL_2]^+[LAuCl][AuCl_2]^-$}, 1. $[Au(SMe_2)Cl]$ (0.3 g, 1.02 mmol) was dissolved in 20 mL of acetonitrile. To the solution was added 1 equiv of 2-aminopyridine (0.096 g, 1.02 mmol), and the solution was stirred at room temperature for 12 h. Addition of excess diethyl ether to the solution gave pure compound **1** as a pale yellow precipitate, yield 63%. Diffusion of diethyl ether into an acetonitrile solution of **1** gave pale yellow crystals. Anal. Calcd for $[C_{15}H_{18}Au_3Cl_3N_6]$: C, 18.38, H, 1.84, N, 8.56. Found: C, 18.16, H, 1.74, N, 8.45. ^{1}H NMR data ($CDCl_3$, 25 °C): δ 8.04−6.66 (12H, br m, H4C5), 5.47 (2H, br s, NH), 4.42 (4H, br s, NH). Compound **1** decomposes at 85 °C.

Crystal Structure Determination of 1. A summary of crystal and data processing parameters for **1** is given in Table 1. A yellow hexagonal block crystal of **1** with a dimension of 0.3 × 0.25 × 0.15 mm was selected, mounted at the end of the glass fiber, and used for diffraction studies. The diffraction experiments were carried out on a Siemens SMART CCD diffractometer with a Mo Kα sealed tube at 23 °C. Preliminary cell constants were obtained from 60 frames (width of 0.3° in ω) data. Final cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. A total of 13574 reflections were collected in the θ range 2.37−29.31° ($-9 \le h \le 14$, $-16 \le k \le 15$, $-24 \le l \le 20$) with a frame width of 0.3° in ω and a counting time of 10 s per frame at a crystal-to-detector distance of 4.95 cm. The collected frames were integrated using the preliminary cell-orientation matrix. The following software packages were used: SMART[12]was used for collecting frames of data, indexing reflection, and determining lattice parameters, SAINT[12] for integration of intensity of reflections and scaling, SADABS[13] for absorption correction, and SHELXTL[14] for space group and structure determination, refinements, graphics, and structure reporting. The space group $P2_1/n$ was unambiguously determined from the systematic absences. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. All the hydrogen atoms except one (H2b attached to N2) were located in the Fourier difference map using the peaks with electron densities ranged from 0.42 to 0.71 e Å^{-3}. They were all placed in their calculated positions and included in the structure factor calculations. The positions of the hydrogen atoms found in the Fourier difference map and calculated positions around NH_2 groups were the same within experimental errors. In the final least-squares refinement cycles on F^2, the model converged at $R1 = 0.0318$, w$R2 = 0.0748$, and goodness of fit = 1.050 for 4393 reflections with $I > 2\sigma(I)$ and 245 parameters, and $R1 = 0.0419$ and w$R2 = 0.0794$ for all 5305 data. In the final difference Fourier synthesis the electron density fluctuations were quite normal and found in the range 1.621 to −0.882 e Å^{-3}. The top 18 peaks were associated with Au atoms at distances in the range of 0.85−1.07 Å.

Results and Discussion

Reacting an acetonitrile solution of $[Au(SMe_2)Cl]$ with 1 equiv of 2-aminopyridine (L) at room temperature for 12 h gives a pale yellow compound with empirical formula [LAuCl]. Diffusion of diethyl ether into an acetonitrile solution of the compound affords pale yellow crystals. Single-crystal structure analysis of **1** shows that there are three different gold(I) complexes in the crystal, namely the cation $[AuL_2]^+$, the neutral complex [LAuCl], and the anion $[AuCl_2]^-$. (Figure 1). It is noted that the X-ray crystal structure of the complex $[(pyrr)_4Au_3Cl_3]$ (pyrr = pyrrolidine)[15] showed that the compound contains neutral complex [(pyrr)AuCl], cation $[Au(pyrr)_2]^+$, and Cl^- ion in the ratio 2:1:1. But as far as we are aware, **1** is the first compound which contains cationic, anionic, and neutral gold(I) species in the same crystal. Apparently, the formation of **1** involves a scrambling of the ligands 2-aminopyridine and chloride ion (reaction 1).

$$3[Au(SMe_2)Cl] + 3L \rightarrow \{[AuL_2]^+[LAuCl][AuCl_2]^-\}\ \mathbf{1} + 3SMe_2 \quad (1)$$

The room temperature ^{1}H NMR spectrum of **1** showed broad signals, indicating there is a rapid exchange of the ligand 2-aminopyridine among the Au(I) complexes in solution, presumably due to the weak Au−N bond. In contrast to 2-aminopyridine; 2-picoline, 3-picoline, and pyridine react with Au(tetrahydrothiophene)Cl to form the neutral complex [Au(2-picoline)Cl][5] and ionic compounds $\{[Au(3\text{-picoline})_2]^+[AuCl_2]^-\}_n$[5] and $\{[Au(pyridine)_2]^+[AuCl_2]^-\}_2$,[4] respectively. The formation of different products from these similar pyridine ligands suggests the equilibrium for the ligand redistribution reaction is very sensitive to factors such as solvent polarity and electronic properties of the pyridine ligand. Notably, a recent study[10] showed that the reaction between $[Au(SMe_2)Cl]$ and $Ph_2C{=}NH$ produced neutral complex $[Au(Ph_2C{=}NH)Cl]$ and ions $[Au(Ph_2C{=}NH)_2]^+$ and $[AuCl_2]^-$. Unlike compound **1**, which contains neutral complex [LAuCl] and ionic compounds $[AuL_2]^+[AuCl_2]^-$ in the same crystal, the complex $[Au(Ph_2C{=}NH)Cl]$ and the ions $[Au(Ph_2C{=}NH)_2]^+[AuCl_2]^-$ crystallized separately, giving two forms of crystals. The cocrystallization of the neutral complex [LAuCl] with the ions $[AuL_2]^+[AuCl_2]^-$ in **1** may be due to favorable secondary interactions such as aurophilic interactions, N−H···Cl hydrogen bonds (*vide infra*), or crystal packing.

Inspection of the crystal structure of compound **1** reveals that the three Au(I) complexes assemble into trinuclear units in which the neutral complex [LAuCl] intercalates between the ions $[AuL_2]^+$ and $[AuCl_2]^-$. The Au−Au distances between the central complex [LAuCl] and the cation $[AuL_2]^+$ [Au(1)−Au(2)] and between the central complex [LAuCl] and the anion $[AuCl_2]^-$ [Au(1)−Au(3)] are 3.3335(3) and 3.2729(4) Å, respectively. These Au−Au distances lie in the normal range of 3.05−3.40 Å observed for intermolecular Au(I)···Au(I)

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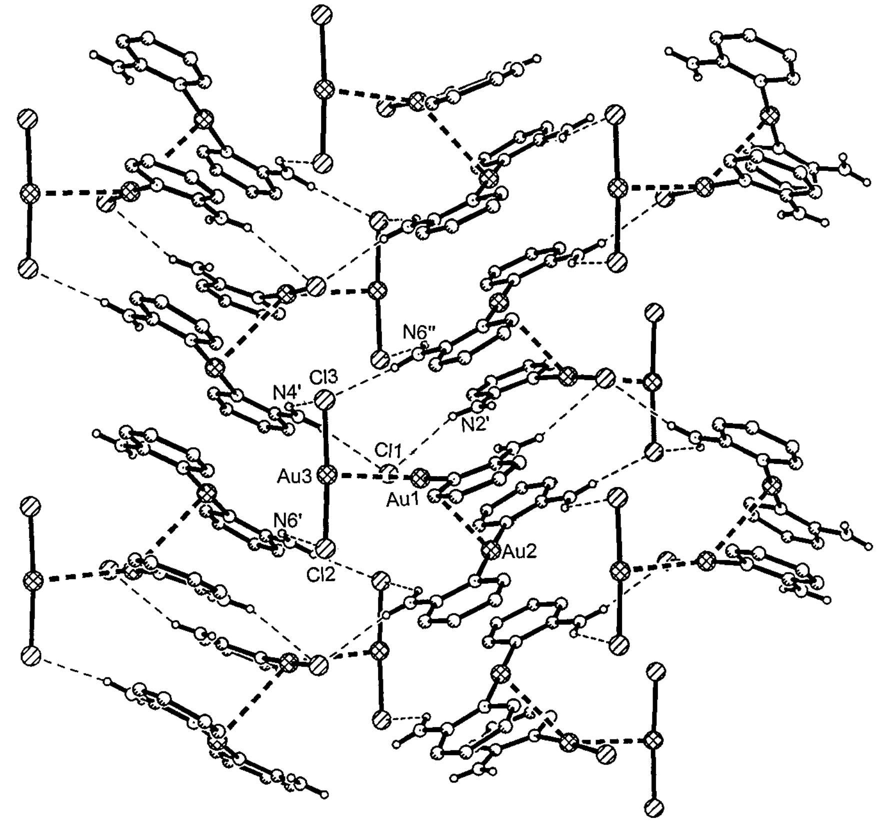

Figure 2. Two-dimensional sheetlike structure in the compound $\{[AuL_2]^+[LAuCl][AuCl_2]^-\}$, **1**. The hydrogen atoms of the NH_2 groups are located in the calculated positions. Intermolecular Cl···N (*N*H_2-pyridine) distance (Å): Cl(1)···N(2′), 3.596; Cl(1)···N(4′), 3.471; Cl(2)···N(6′), 3.382; Cl(3)···N(4′), 3.309; Cl(3)···N(6″), 3.382.

interaction,[17] indicating the three Au(I) complexes in the trinuclear units are held together by weak aurophilic attraction. On the other hand, there is no Au(I)···Au(I) contact between trinuclear units as all the Au−Au separations between two adjacent trinuclear units are longer than 4 Å. All three Au(I) complexes are essentially linear and the lengths of the Au−Cl and Au−N bonds are normal. Moreover, the two NH_2 groups in the cation $[AuL_2]^+$ are oriented trans to each other. Notably, the arrangement of three gold atoms in the trinuclear unit deviates substantially from linearity with the Au(3)−Au(1)−Au(2) angle of 138.196(11)°. The three Au(I) complexes are all staggered. The dihedral angle between the central complex [LAuCl] and the cation $[AuL_2]^+$ is 46.04(0.17)° [Cl(1)−Au(1)−Au(2)−N(5)], indicating there is no $\pi-\pi$ interaction between the two 2-aminopyridine ligands of [LAuCl] and $[AuL_2]^+$. The anion $[AuCl_2]^-$ is almost perpendicular to the complex [LAuCl] [Cl(1)−Au(1)−Au(3)−Cl(2) 91.58(0.07)°]. Perhaps the most remarkable structural feature of **1** is the unprecedented pattern [+ neutral −] of the three different gold(I) complexes in the trinuclear unit. Considering the Coulombic interaction, one would expect the ions $[AuL_2]^+$ and $[AuCl_2]^-$ to be placed together, forming an ion pair (+ −). In fact, the ion pair (+ −) appears in the solid-state structures of all reported $\{[AuL'_2]^+[AuX_2]^-\}$ compounds.[3−6,18] Therefore it is rather surprising to find that the ions $[AuL_2]^+$ and $[AuCl_2]^-$ are separated in **1**. The [+ neutral −] arrangement in **1** clearly indicates that electrostatic interaction is not a dominant factor in controlling the solid state arrangements of ionic Au(I) complexes. It should be noted that a similar conclusion has been reached from recent theoretical calculations[19] and structural studies.[7,20] The aurophilic interactions between the Au(I) species in **1** are weak, as evidenced by the relatively long Au···Au distances. Accordingly, the Coulombic attraction between the cation $[AuL_2]^+$ and the anion $[AuCl_2]^-$ is overruled by other secondary interactions such as hydrogen bonds (*vide infra*) rather than aurophilicity.

Close examination of the X-ray crystal structure of **1** shows that the trinuclear gold(I) units assemble into a two-dimensional sheetlike structure in the solid state (Figure 2). The three chloride ligands in a trinuclear gold(I) unit are directed toward the NH_2 groups from adjacent trinuclear units. The Cl(3) of the $[AuCl_2]^-$ in a trinuclear unit is close to two NH_2 groups from the cations $[AuL_2]^+$ in two adjacent trinuclear units, whereas the Cl(2) is in contact with an NH_2 group from a neighboring $[AuL_2]^+$ ion. In addition, the Cl(1) of the complex [LAuCl] is close to the NH_2 groups of $[AuL_2]^+$ and [LAuCl] from two different trinuclear units. The coexistence of the N−H···Cl hydrogen bond and the aurophilic interactions has been observed in the compounds $\{[Au(Ph_2C{=}NH)_2]^+[AuCl_2]^-\}$[16] and $[(Cy_2NH)AuCl]$ (Cy = cyclohexyl).[10b] The intermolecular N···Cl distances found in compound **1**, ranging from 3.309 to 3.595 Å, compare favorably with those in $\{[Au(Ph_2C{=}NH)_2]^+[AuCl_2]^-\}$ (N···Cl = 3.377, 3.443 Å) and $[(Cy_2NH)AuCl]$ (N···Cl = 3.391(8) Å). This indicates the existence of N−H···Cl hydrogen bonds between the NH_2 groups of the ligand 2-aminopyridine

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(donor) and the chloride ions in the complexes [LAuCl] and $[AuCl_2]^-$ (acceptor). The extensive N−H···Cl hydrogen bonds and aurophilic interactions in **1** account for the extended two-dimensional sheetlike structure observed in the crystal. Besides, the observed pattern [+ neutral −] in **1** could be due to the fact that the Coulombic attraction between the cation and the anion is overridden by the extensive N−H···Cl hydrogen bonds and weak aurophilic interactions.

Recently there has been a growing interest in engineering the crystal structures of transition metal complexes by using more than one kind of secondary intermolecular interaction.[21] For example, Schmidbaur has demonstrated that aurophilicity and hydrogen bond, which have similar bond energy, can work cooperatively in assembling gold(I) complexes into dimers and oligomers.[22] Similarly, $\pi-\pi$ interactions between polypyridine ligands and hydrogen bonds have been employed to arrange cyclometalated platinum(II) complexes in one-dimensional chains.[23] The present compound features the first example in which the extended two-dimensional structure of Au(I) complexes arises from cooperative actions of aurophilicity and N−H···Cl hydrogen bonds. It is noted that Che and co-workers observed extended two-dimensional structures of Au(I) complexes in the crystals of polynuclear Au(I) compounds $[(L''Au)(AuPPhMe_2)_2]_2$ (H_3L'' = trithiocyanuric acid)[24a] and [(AuX′)(L1)] (X′ = Cl, Br, I, and L1 = 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane).[24b] However, the Au(I) species in the two compounds are held together solely by aurophilic attraction. Several recent studies suggested that the exceptional stability of several Au^I-amine[10b,c] or -ketimine[10a,16] complexes is probably due to intermolecular N−H···O/Cl/Br hydrogen bonds. For example, the X-ray crystal structure of the complex $[Au(NH{=}CMe_2)_2]^+[CF_3SO_3]^-$ showed that the cations $[Au(NH{=}CMe_2)_2]^+$ aggregate into one-dimensional polymers in the solid state with the ligand's acetimine hydrogen bonded to the anion trifluorosulfonate $[N-H\cdots O(CF_3SO_3)]$.[10a] The N−H···O hydrogen bonds are suggested to be responsible for the exceptional stability of the complex and the formation of the polymer of cations. Similarly, the extensive aurophilic and N−H···Cl hydrogen bonding interactions in **1** would provide stabilization to the compound. The additional stabilization may account for the unusual cocrystallization of the complex [LAuCl] with the ions $[AuL_2]^+[AuCl_2]^-$ in **1**. The solid of compound **1** is not photoluminescent at room temperature or 77 K.

Conclusion

In summary we have demonstrated that the reaction between $[Au(SMe_2)Cl]$ and 2-aminopyridine leads to the formation of three different gold(I) complexes, [LAuCl], $[AuL_2]^+$ and $[AuCl_2]^-$. The neutral complex [LAuCl] cocrystallizes with ionic compounds $[AuL_2]^+$ and $[AuCl_2]^-$ to form an unprecedented pattern [+ neutral −] in the solid state. The segregation of the cation $[AuL_2]^+$ and the anion $[AuCl_2]^-$ in the trinuclear gold(I) unit indicates that electrostatic attraction is not a crucial factor in determining the solid state arrangement of ionic Au(I) complexes. We also have shown that aurophilcitiy and N−H···Cl hydrogen bonds can work cooperatively to form the extended two-dimensional sheetlike structure of Au(I) complexes.

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Supporting Information Available: Tables of crystallographic data collection parameters, atomic coordinates, and a complete listing of bond lengths and bond angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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