

X-ray Crystallographic Studies of the Products of Oxidative Additions of Iodine to Cyclic Trinuclear Gold(I) Complexes: Directional Effects for Au–I⋯I–Au Interactions

Jess C. Vickery[†] and Alan L. Balch*

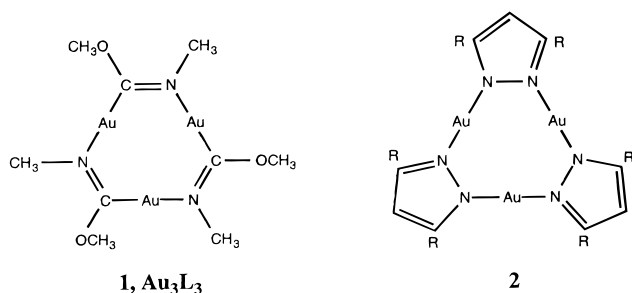
Department of Chemistry, University of California, Davis, California 95616

Received May 22, 1997[⊗]

The crystal structures of cyclic trinuclear organogold compounds, $\text{Au}_3\text{I}_n(\text{CH}_3\text{N}=\text{COCH}_3)_3$ ($n = 2, 4, 6$) reveal that pairs of iodine atoms are added successively to each of the gold atoms in the triangular complexes. Deep red needles of $\text{Au}_3\text{I}_6(\text{CH}_3\text{N}=\text{COCH}_3)_3 \cdot \text{CH}_2\text{Cl}_2$ crystallize in the monoclinic space group $P2_1/c$, with $a = 14.762(4)$ Å, $b = 8.723(3)$ Å, $c = 22.278(6)$ Å, and $\beta = 91.58(2)^\circ$ at 123 K with $Z = 4$. Refinement of 6591 reflections and 164 parameters yielded $R = 0.055$. The structure consists of columns of the molecular units united by weak iodine⋯iodine interactions which range in length from 3.636(2) to 3.716(2) Å. Within the molecular unit, all iodine⋯iodine distances are well beyond the sum of their van der Waals radii and fall in the range from 3.965(2) to 4.211(2) Å. The gold coordination is significantly distorted from planarity with I–Au–I angles of ca. 163° . In $\text{Au}_3\text{I}_6(\text{CH}_3\text{N}=\text{COCH}_3)_3$ the intermolecular I⋯I interactions are significantly shorter than the intramolecular I⋯I contacts. Red parallelepipeds of the tetraiodo complex, $\text{Au}_2\text{I}_4\text{Au}(\text{CH}_3\text{N}=\text{COCH}_3)_3$, crystallize in the triclinic space group $P\bar{1}$, with $a = 7.404(2)$ Å, $b = 9.278(2)$ Å, $c = 16.331(3)$ Å, $\alpha = 80.77(3)^\circ$, $\beta = 78.68(3)^\circ$, and $\gamma = 81.85(3)^\circ$ at 123 K with $Z = 2$. Refinement of 4963 reflections and 124 parameters yielded $R = 0.048$. No noteworthy intermolecular contacts are present in this compound. Orange-red hexagonal plates of the diiodo complex, $\text{AuI}_2\text{Au}_2(\text{CH}_3\text{N}=\text{COCH}_3)_3$, crystallize in the monoclinic space group $P2_1/c$, with $a = 9.309(4)$ Å, $b = 13.597(4)$ Å, $c = 14.899(5)$ Å, and $\beta = 101.26(3)^\circ$ at 123 K with $Z = 4$. Refinement of 4133 reflections and 121 parameters yielded $R = 0.064$. This structure consists of discrete molecular units displaying no noteworthy inter- or intramolecular contacts.

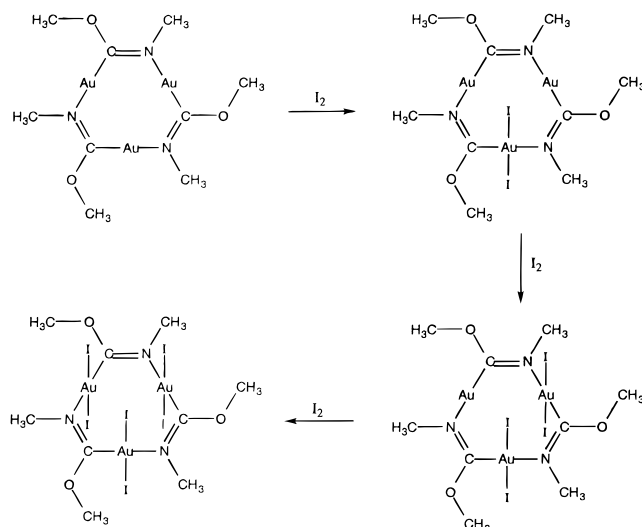
Introduction

Recent reports of novel physical properties—solvoluminescence,¹ supramolecular association,¹ and formation of columnar mesophases²—have brought renewed attention to the class of trinuclear gold(I) complexes exemplified by complexes **1**³ and **2**.⁴ Colorless crystals of complex **1** are readily obtained



by addition of potassium hydroxide in methanol and methyl isocyanide to a solution of Ph_3PAuCl .³ When these crystals are photoirradiated with near-UV light, they produce a yellow phosphorescence. Contact of the phosphorescing crystals by a solvent such as dichloromethane or chloroform produces a burst of light that is readily detected by the human eye.¹ This latter phenomenon has been termed solvoluminescence. This lumi-

Scheme 1



nescence has been attributed to charge separation and electron mobility along the columnar arrangements of molecules of complex **1** that are present in the solid. In order to thoroughly understand the properties of complex **1** that might contribute to the solvoluminescence, we have undertaken a careful study of its redox chemistry.

Some time ago this laboratory reported that the stepwise addition of diiodine (or dibromine) to complex **1** resulted in the formation of three types of compounds: $\text{AuX}_2\text{Au}_2\text{L}_3$, $\text{Au}_2\text{X}_4\text{AuL}_3$, and $\text{Au}_3\text{X}_6\text{L}_3$.⁵ The structures set out in Scheme 1 were proposed for these compounds on the basis of ¹H NMR and infrared spectroscopic characterization. In the meantime reports

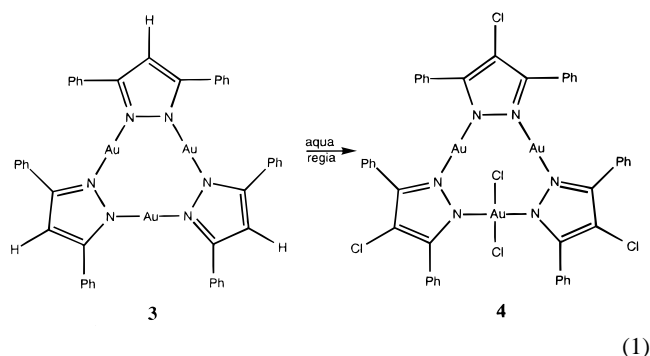
[†] Present address: Department of Chemistry, California State University, Chico, Chico, CA 95929.

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1997.

- (1) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179.
- (2) Barberá, J.; Elduque, A.; Giménez, R.; Oro, L. A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2832.
- (3) Parks, J. E.; Balch, A. L. *J. Organomet. Chem.* **1974**, *71*, 453.
- (4) Minghetti, G.; Bonati, F. *Inorg. Chem.* **1974**, *13*, 1600.
- (5) Tiripicchio, A.; Camellini, M. T.; Minghetti, G. *J. Organomet. Chem.* **1979**, *171*, 399.

(5) Balch A. L.; Doonan, D. J. *J. Organomet. Chem.* **1977**, *131*, 137.

of a few other such mixed-oxidation state materials have appeared.^{6,7} Recent developments have, however, suggested that the structures of these compounds warranted further examination. The formation of Au–Au bonds, an idea discussed but rejected in the initial characterization of the Au₃L₃ oxidation products,⁵ has been shown to be an important reaction in ligand-bridged gold(I) complexes.⁸ Stable complexes of the rare oxidation state, Au(II), which might be present in the oxidized trimers, have been isolated recently.⁹ Most significantly to the present investigation, Fackler and co-workers have reported that oxidation of the related pyrazolato-bridged compound **3** with aqua regia forms the mixed valence Au^{III}Au^I₂ complex **4**, as shown in eq 1.¹⁰ The oxidative–addition reaction was ac-



companied by chlorination of the bridging groups. Remarkably, however, further addition of chlorine or other oxidation did not occur under the rather harsh conditions used. Additionally, oxidation of related, alkyl substituted pyrazolato-bridged trimers with molecular iodine was also reported to stop with the addition of 1 equiv to form Au₂Au₂(3,5-R₂pz)₃ (pz = pyrazene).^{11,12} These observations lead us to question the factors that could inhibit oxidation within these triangular complexes. Would contact between the added halogens destabilize structures such as those proposed for Au₂X₄AuL₃ and Au₃X₆L₃? Might Au₃I₆L₃ be, in actuality, [Au₃L₃](I₃)₂? Consequently, crystallographic characterization of this set of complexes was undertaken. We focused on the iodide compounds since these would involve the greatest problems with steric crowding. We were also interested in the effects of oxidation upon the intermolecular Au···Au contacts that result in the formation of trigonal prismatic columns of complex **1** in the solid state. Separations of Au(I) centers of less than 3.6 Å are viewed as resulting from attractive interactions that are, in part, due to relativistic effects.^{13–15} In complex **1** the intramolecular Au···Au distance is 3.308(2) Å, while the intermolecular Au···Au distance is only slightly longer, 3.346(1) Å.¹ Would these intermolecular Au···Au interactions that result from aurophilicity persist in the oxidation products?

- (6) Bonati, F.; Brurini, A.; Pietroni, B. R.; Bovio, B. *J. Organomet. Chem.* **1991**, *408*, 271.
 (7) Bovio, B.; Calogero, S.; Wagner, F. E.; Burini, A.; Pietroni, B. P. *J. Organomet. Chem.* **1994**, *470*, 275.
 (8) Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 1.
 (9) Elder, S. H.; Lucier, G. M.; Hollander, F. J.; Bartlett, N. *J. Am. Chem. Soc.* **1997**, *119*, 1020. Hwang, F. G.; Hwang, G.; Lee, K. C.; Mistry, F.; Phillips, P. S.; Willner, H.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 1271.
 (10) Raptis R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 5003.
 (11) Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658.
 (12) Katada, M.; Sato, K.; Uchida, Y.; Iijima, S.; Sano, H.; Wei, H. H.; Sakai, H.; Maeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 945.
 (13) Jones, P. G. *Gold Bull.* **1981**, *14*, 102.
 (14) Schmidbaur, H. *Interdisip. Sci. Rev.* **1992**, *17*, 213.
 (15) Pathaneni, S. S.; Desiraju, G. R. *J. Chem. Soc., Dalton Trans.* **1993**, 319.

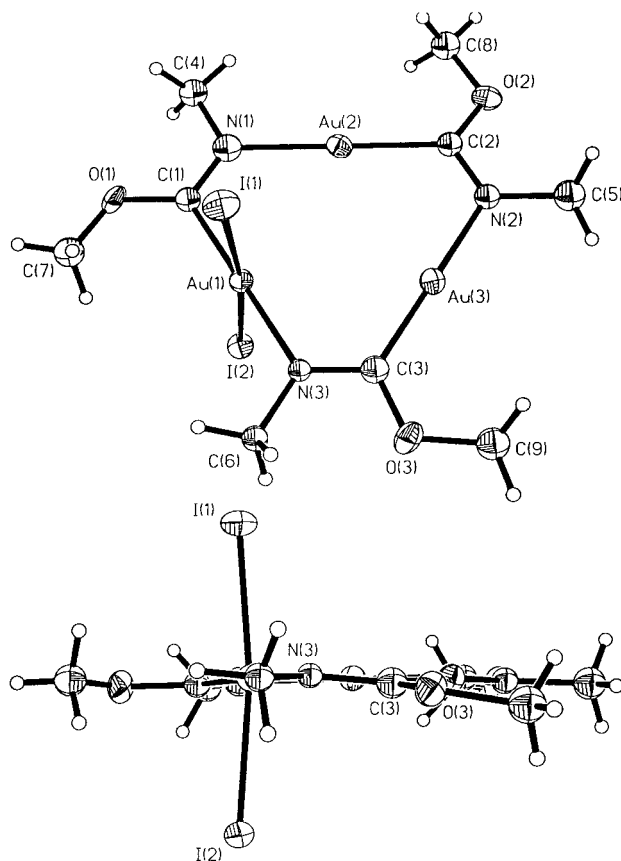


Figure 1. Two views of Au₂Au₂L₃ with 50% thermal contours.

Results

Au₂Au₂L₃, Au₂I₄AuL₃, and Au₃I₆L₃ were prepared as described previously.⁵ None showed any evidence for the solvoluminescence that is so readily observed for Au₃L₃.¹ No EPR signals were observed for these iodo complexes, and hence there is no spectroscopic evidence for Au(II) centers.

Au₂Au₂L₃. Figure 1 shows a drawing of the entire molecule, which has no crystallographically imposed symmetry. Selected interatomic distances and angles for this and other complexes are given in Table 1, where comparisons among the five structures are facilitated. The structure of Au₂Au₂L₃ has the core trimer structure of complex **1** intact with two iodide ligands added to a single gold atom as originally proposed.⁵ The coordination about Au(2) and Au(3) is linear, while Au(1) has somewhat distorted planar geometry. The C(1)–Au(1)–N(3) portion is nearly linear, but the I(1)–Au–I(2) angle is somewhat bent. There are no attractive Au···Au contacts between individual molecules. The shortest intermolecular Au···Au distance is 5.137(2) Å.

Au₂I₄AuL₃. Crystallization of Au₂I₄AuL₃ was complicated by the occurrence of disproportionation during crystal growth. The ¹H NMR spectrum of a solution of chloroform-*d* Au₂I₄AuL₃ that contained approximately 1.6% of Au₃I₆L₃ and no detectable Au₂I₂AuL₃ showed no sign of disproportionation over a 14 day period. However, when a portion of this sample was evaporated to induce crystallization (over an additional 4 week period), crystals of three complexes—Au₂Au₂L₃ as orange-red plates, Au₂I₄AuL₃ as red parallelepipeds, and Au₃I₆L₃ in the form of deep red needles—were clearly present. Thus, the disproportionation reaction shown in eq 2 occurs during the

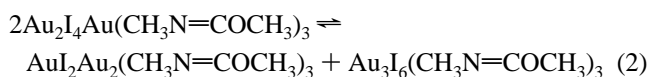


Table 1. Selected Interatomic Distances and Angles

| | Au ₃ L ₃ | AuI ₂ Au ₂ L ₃ | Au ₂ I ₄ AuL ₃ | Au ₃ I ₆ L ₃ ·CH ₂ Cl ₂ |
|--------------------|--------------------------------|---|---|--|
| | | Distances (Å) | | |
| Au(1)···Au(2) | 3.308(2) [†] | 3.303(2) | 3.460(1) | 3.441(1) |
| Au(1)···Au(3) | 3.308(2) [†] | 3.356(2) | 3.3158(11) | 3.414(1) |
| Au(2)···Au(3) | 3.308(2) [†] | 3.286(2) | 3.2937(13) | 3.402(1) |
| I(1)···I(3) | | | 4.020(2) | 4.086(2) |
| I(1)···I(5) | | | | 4.211(2) |
| I(2)···I(4) | | | 4.099(2) | 4.193(2) |
| I(2)···I(6) | | | | 3.965(2) |
| I(3)···I(5) | | | | 4.080(2) |
| I(4)···I(6) | | | | 4.045(2) |
| I(1)···I(2)′ | | | | 3.636(2) |
| I(3)···I(4)′ | | | | 3.708(2) |
| I(5)···I(6)′ | | | | 3.716(2) |
| Au(1)–I(1) | | 2.622(2) | 2.6169(14) | 2.635(2) |
| Au(1)–I(2) | | 2.627(2) | 2.6206(14) | 2.629(2) |
| Au(2)–I(3) | | | 2.6305(14) | 2.626(2) |
| Au(2)–I(4) | | | 2.6238(13) | 2.634(2) |
| Au(3)–I(5) | | | | 2.626(2) |
| Au(3)–I(6) | | | | 2.622(2) |
| Au(1)–C(1) | 2.000(10) ^{††} | 2.03(2) | 2.02(2) | 2.03(2) |
| Au(1)–N(3) | 2.032(10) ^{†††} | 2.07(2) | 2.072(12) | 2.08(2) |
| Au(2)–C(2) | 2.000(10) ^{††} | 2.02(2) | 2.01(2) | 2.00(2) |
| Au(2)–N(1) | 2.032(10) ^{†††} | 2.07(2) | 2.095(12) | 2.076(14) |
| Au(3)–C(3) | 2.000(10) ^{††} | 1.97(2) | 2.01(2) | 2.06(2) |
| Au(3)–N(2) | 2.032(10) ^{†††} | 2.05(2) | 2.065(13) | 2.074(13) |
| | | Angles (deg) | | |
| Au(1)–Au(2)–Au(3) | 60.0* | 61.23(4) | 58.75(3) | 59.85(3) |
| Au(2)–Au(3)–Au(1) | 60.0* | 59.63(3) | 63.13(3) | 60.65(3) |
| Au(3)–Au(1)–Au(2) | 60.0* | 59.13(3) | 58.12(3) | 59.50(3) |
| I(1)–Au(1)–I(2) | | 172.61(6) | 167.88(4) | 162.55(5) |
| I(3)–Au(2)–I(4) | | | 163.13(4) | 162.77(5) |
| I(5)–Au(3)–I(6) | | | | 163.16(5) |
| Au(1)–I(1)···I(2)′ | | | | 154.14(5) |
| Au(1)–I(2)···I(1)′ | | | | 166.03(5) |
| Au(2)–I(3)···I(4)′ | | | | 164.86(5) |
| Au(2)–I(4)···I(3)′ | | | | 147.67(5) |
| Au(3)–I(5)···I(6)′ | | | | 150.72(5) |
| Au(3)–I(6)···I(5)′ | | | | 160.08(5) |
| Au(1)–C(1)–N(1) | 120(4)** | 118(2) | 119.8(11) | 119.1(13) |
| Au(2)–C(2)–N(2) | 120(4)** | 120(2) | 117.1(11) | 117.5(12) |
| Au(3)–C(3)–N(3) | 120(4)** | 123(2) | 121.8(11) | 117.3(13) |
| Au(1)–N(3)–C(3) | 121(4)*** | 118(2) | 118.6(11) | 124.6(12) |
| Au(2)–N(1)–C(1) | 121(4)*** | 121(2) | 124.1(11) | 124.6(13) |
| Au(3)–N(2)–C(2) | 121(4)*** | 119(2) | 121.9(10) | 123.9(11) |

^a †, ††, †††, *, **, and *** denote groups of parameters that are equivalent because of crystallographic symmetry.

crystallization. Factors such as the relative solubilities of the three complexes, the rates of nucleation, and rates of crystal growth of each of these solids are likely to be responsible for the complexity of the crystal growth process. Nevertheless, sufficiently large crystals of the desired material, which was the most abundant crystalline form present, were obtained. Further crystallographic studies were performed on the other two crystalline products, and their identity was verified unequivocally as AuI₂Au₂L₃ and Au₃I₆L₃, respectively.

Figure 2 shows a drawing of the molecule. Again the planar Au₃L₃ core is present. The four iodide ligands have added to two of the three gold atoms. While the molecule lacks any crystallographically imposed symmetry, there is a virtual mirror plane that passes through the three gold atoms. The coordination of Au(3) is linear, while Au(1) and Au(2) have approximately planar geometry. However, there is a distortion of the trans I–Au–I angles which are bent by ca. 12–16° from linearity, while the C–Au–N angles are nearly linear. As with the preceding compound, there are no short Au···Au contacts. The closest contact between two gold centers in different molecules is 5.692(2) Å.

Au₃I₆L₃·CH₂Cl₂. Figure 3 shows a perspective view of the molecule. Although the complex lacks crystallographic sym-

metry, it has virtual *C*_{3*h*} symmetry with the pseudo-*C*₃ axis passing through the center of the Au₃ triangle. Again the Au₃L₃ core is nearly planar with the iodide ligands attached pairwise to each gold atom and arranged nearly perpendicularly to the Au₃ triangle. Each gold atom has roughly planar coordination with, however, significant bending of the I–Au–I angles away from linearity. There is no unusual contact between the dichloromethane molecule and the trigold complex. However, the molecules do pack in an interesting way, as shown in Figure 4. The molecules form columns in which the closest approaches involve intermolecular I···I contacts. The individual triangular complexes eclipse one another. Thus, the stacking is reminiscent of that found in complex **1**, but with the addition of the iodide ligands, the separation between Au₃ planes is now 8.732(2) Å in Au₃I₆L₃·CH₂Cl₂, whereas it is 3.346(1) Å in complex **1**.¹ The stacks do not all run parallel to one another. Rather one stack is offset at an angle to another, as can be seen in Figure 4.

Another form of this complex, Au₃I₆L₃·CHCl₃, has been obtained from diffusion of methanol into a chloroform solution of the complex. The molecular structure and the packing into columns with short intermolecular I···I contacts are similar to those features in Au₃I₆L₃·CH₂Cl₂.

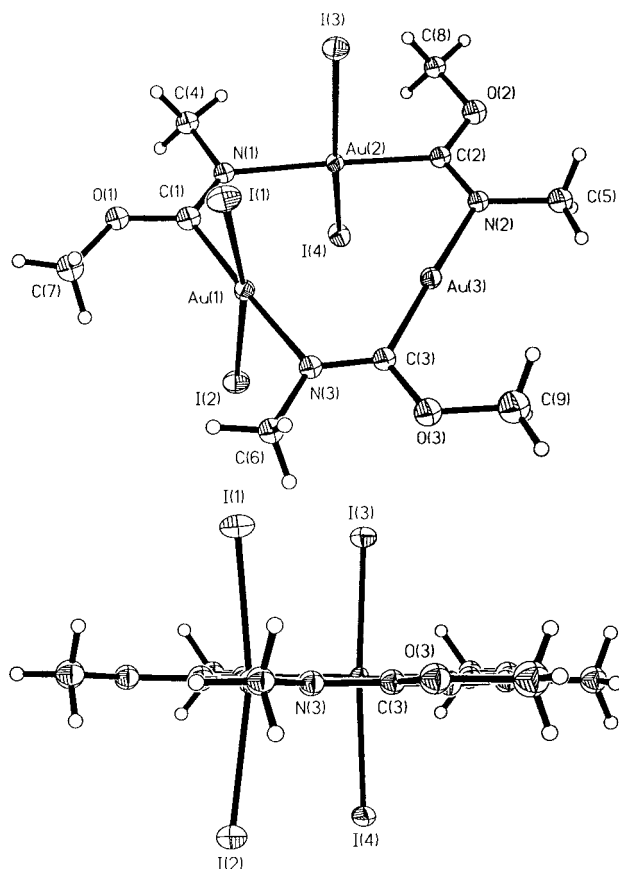


Figure 2. Two views of $\text{Au}_2\text{I}_4\text{AuL}_3$ with 50% thermal contours.

Discussion

The crystallographic results show that the structures originally proposed for these complexes are correct. In the oxidative addition reactions, diiodine molecules are added sequentially to each of the gold atoms. No gold-gold bonds are formed, and there is no evidence for the formation of Au(II) centers. Throughout the set of complexes the basic skeleton comprised of the three gold atoms and the three bridging ligands retains its structure. The variation in intramolecular $\text{Au}\cdots\text{Au}$ separations is small. There is, however, a trend toward increasing $\text{Au}\cdots\text{Au}$ separations as more iodine is added to the complex. Thus, in $\text{Au}_2\text{I}_2\text{Au}_2\text{L}_3$ the $\text{Au}(2)\cdots\text{Au}(3)$ distance which involves two Au(I) centers is shorter than the other two $\text{Au}\cdots\text{Au}$ distances which involve an Au(I) and an Au(III) center. In $\text{Au}_2\text{I}_4\text{AuL}_3$ the $\text{Au}(1)\cdots\text{Au}(2)$ distance which involves two Au(III) centers is longer than the other two $\text{Au}\cdots\text{Au}$ distances which involve an Au(III) and an Au(I) center. Moreover, the $\text{Au}\cdots\text{Au}$ distances in the two forms of $\text{Au}_3\text{I}_6\text{L}_3$ which involve two Au(III) centers are longer than any of the $\text{Au}\cdots\text{Au}$ distances that involve Au(I) centers in the above compounds, as well as in the parent organogold trimer (1), Au_3L_3 . Nevertheless, the C-Au-N angles (which fall in the narrow range $176.3\text{--}180^\circ$) vary little from 180° .

The Au-I distances all fall in a range of $2.614(6)\text{--}2.633(7)$ Å and are commensurate with literature values for terminal Au-I bonds. For example in the closely related complex, **5**, the Au-I distances are $2.595(4)$ and $2.601(5)$ Å.⁷ However, for all of the complexes reported here the I-Au-I angles deviate significantly from linearity. In the least sterically crowded molecule, $\text{Au}_2\text{I}_2\text{Au}_2\text{L}_3$, the I-Au-I angle is $172.61(6)^\circ$ and the iodide ligands are bent away from the core of the molecule. For comparison, the I-Au-I angle in complex **5** is $175.8(1)^\circ$,⁷ and the Cl-Au-Cl angle in the related mixed valence trimer, **4**, is $178.7(3)^\circ$.¹⁰ The bending of the I-Au-I

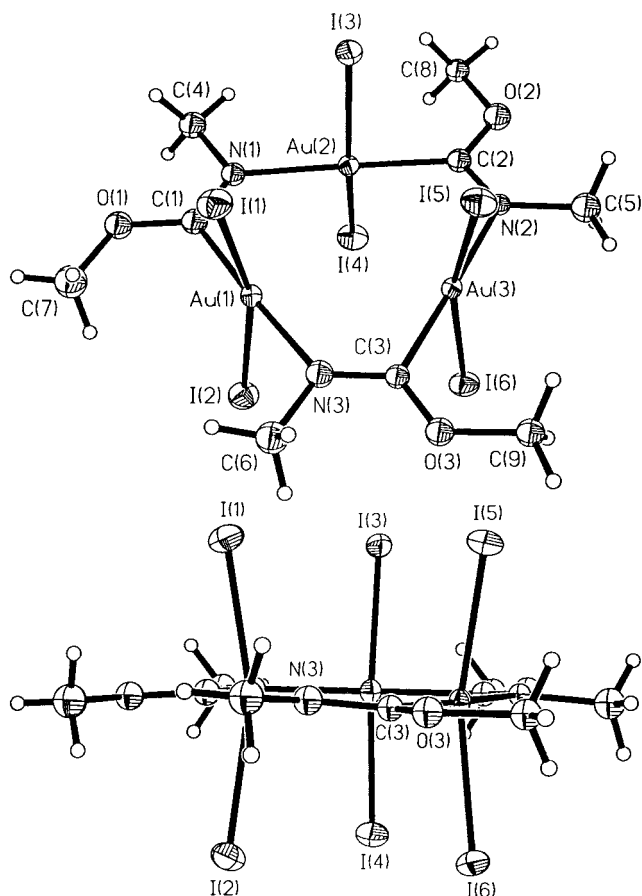
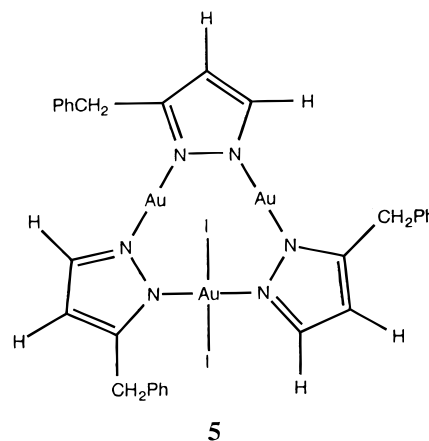


Figure 3. Two views $\text{Au}_3\text{I}_6\text{L}_3\cdot\text{CH}_2\text{Cl}_2$ with 50% thermal contours.



angle in $\text{Au}_2\text{I}_2\text{Au}_2\text{L}_3$ and in complex **5** must result from repulsion of the iodide by other parts of the trimer. The four nonbonded $\text{Au}\cdots\text{I}$ distances range from $4.225(2)$ to $4.411(2)$ Å. In comparison, the sum of the van der Waals radii for gold and iodine is 3.78 Å. In $\text{Au}_2\text{I}_4\text{AuL}_3$ and $\text{Au}_3\text{I}_6\text{L}_3$, where $\text{I}\cdots\text{I}$ contacts become significant, the I-Au-I angles are narrowed further. In $\text{Au}_2\text{I}_4\text{AuL}_3$ these angles are $167.88(4)^\circ$ and $163.13(4)^\circ$. In the hexaiodide complex, the I-Au-I angles fall in the range $163.2(2)^\circ\text{--}162.5(2)^\circ$. This marked bending of the I-Au-I angles must be largely a consequence of the repulsive intramolecular $\text{I}\cdots\text{I}$ contacts. The van der Waals radius of iodide is taken as 1.98 Å,¹⁶ so contacts less than 3.96 Å demonstrate attractive interactions between terminal iodide moieties. In the $\text{Au}_3\text{I}_6\text{L}_3$ structure, the intramolecular $\text{I}\cdots\text{I}$ contacts range from $3.965(2)$ to $4.211(2)$ Å. Thus, these contacts are responsible for the bending of the I-Au-I units.

(16) Desiraju, G. R.; Parthasarathy, R. *J. Am. Chem. Soc.* **1989**, *111*, 8725.

Table 2. Crystal Structure Data

| | AuI ₂ Au ₂ L ₃ | Au ₂ I ₄ AuL ₃ | Au ₃ I ₆ L ₃ ·CH ₂ Cl ₂ |
|---|---|---|--|
| formula | C ₉ H ₁₈ Au ₃ I ₂ N ₃ O ₃ | C ₉ H ₁₈ Au ₃ I ₄ N ₃ O ₃ | C ₁₀ H ₂₀ Au ₃ Cl ₂ I ₆ N ₃ O ₃ |
| fw | 1060.96 | 1314.76 | 1653.49 |
| space group | <i>P</i> 2 ₁ / <i>c</i> , monoclinic | <i>P</i> 1, triclinic | <i>P</i> 2 ₁ / <i>c</i> , monoclinic |
| <i>a</i> (Å) | 9.309(4) | 7.404(2) | 14.762(4) |
| <i>b</i> (Å) | 13.597(4) | 9.278(2) | 8.723(3) |
| <i>c</i> (Å) | 14.899(5) | 16.331(3) | 22.278(6) |
| α (deg) | 90 | 80.77(3) | 90 |
| β (deg) | 101.26(3) | 78.68(3) | 91.58(2) |
| γ (deg) | 90 | 81.85(3) | 90 |
| <i>V</i> (Å ³) | 1849.5(11) | 1078.8(4) | 2868(2) |
| <i>T</i> (K) | 123(2) | 123(2) | 123(2) |
| <i>Z</i> | 4 | 2 | 4 |
| <i>d</i> _{calc} (Mg/m ³) | 3.810 | 4.048 | 3.830 |
| radiation, λ (Mo K α) (Å) | 0.710 73 | 0.710 73 | 0.710 73 |
| μ (mm ⁻¹) | 27.084 | 26.084 | 21.972 |
| <i>R</i> ^a | 0.0639 (2876) | 0.0485 (4059) | 0.0549 (4441) |
| <i>R</i> _{w2} ^b | 0.1577 (4133) | 0.1391 (4963) | 0.1365 (6591) |

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ (observed data, $I > 2\sigma(I)$). ^b $R_{w2} = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ (all data).

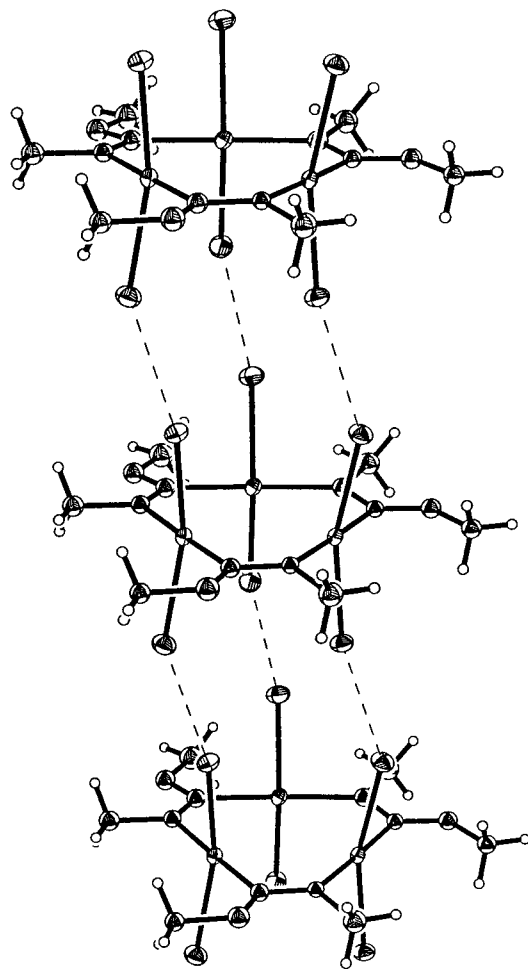


Figure 4. Molecular packing in crystalline Au₃I₆L₃·CH₂Cl₂ showing the formation of columns through I···I interactions.

Intriguingly, the structure of Au₃I₆L₃·CH₂Cl₂ shows the formation of columns in which the triangular complexes display short intermolecular I···I contacts, as seen in Figure 4. *These intermolecular contacts are shorter than the intramolecular I···I contacts listed above.* In Au₃I₆L₃·CH₂Cl₂ the intermolecular I···I separations within the columns fall in the range 3.636(2) to 3.716(2) Å and are 0.3–0.5 Å shorter than the intramolecular I···I separations. This situation demonstrates that the nature of the interaction between terminal iodide ligands has a clear directional component, with an attractive interaction allowed by the end on approach of the two ligands. The side by side

orientation of two iodide ligands obviously results in repulsion since it is accompanied in these complexes by severe bending of the I–Au–I bonds. The existence of solid state interactions in organoiodo compounds has long been a major subject of debate,^{16–24} and it has tentatively been concluded that these compounds display attractive I···I interactions which also depend upon geometry.¹⁶ In this case, there are two preferred geometrical arrangements for attractive halogen···halogen interactions:²⁰ one in which the two C–X···X angles within the C–X···X–C moiety are equal to each other (and approximately 160°) and one in which one of the angles is equal to 180° while the other is 90°. The debate surrounding these close halogen contacts has centered upon whether they originate from attractive forces inherent to the halogen (which depends greatly on relative orientation) or whether the close contacts are merely a manifestation of close packing of nonspherical objects whose van der Waals radii depend upon the relative orientation toward nearest neighbors. Concerning the intra- and intermolecular I···I interactions with the two Au₃I₆L₃ structures, the repulsive intramolecular interactions correspond to Au–I···I units in which are both angles essentially equal to 90°, while the attractive Au–I···I intermolecular contacts correspond to the geometric case where the two Au–I···I angles within the Au–I···I–Au unit are essentially equal to each other (and approach 160°). These observations lend great support to the conclusions of Desiraju^{16,17} and demonstrate that the geometrical dependence observed for organoiodide compounds extends analogously to gold–iodide complexes.

Unlike the hexaiodo complex, the solid state molecular packings of AuI₂Au₂L₃ and Au₂I₄AuL₃ reveal no unusual features. There are no Au···Au contacts less than 3.5 Å and no unusually short Au···I or I···I contacts.

Experimental Section

Preparation of Compounds. AuI₂Au₂L₃, Au₂I₄AuL₃, and Au₃I₆L₃ were prepared as described previously.⁵

- (17) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311.
- (18) Navon, O.; Bernstein, J.; Khodorkovsky, V. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 601.
- (19) Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308.
- (20) Sakurai, T.; Sundaralingam, M.; Jeffrey, G. A. *Acta Crystallogr.* **1963**, *16*, 354.
- (21) Nyburg, S. C.; Faerman, C. H. *Acta Crystallogr.* **1985**, *B41*, 274.
- (22) Nyburg, S. C.; Wong-Ng, W. *Proc. R. Soc. London* **1979**, *A367*, 29.
- (23) Price, S. L.; Stone, A. J. *J. Phys. Chem.* **1988**, *92*, 3325.
- (24) Price, S. L.; Stone, A. J. *Mol. Phys.* **1982**, *1457*.

X-ray Data Collection. $\text{AuI}_2\text{Au}_2\text{L}_3$. Orange-red hexagonal plates were grown by diffusion of diethyl ether into a methylene chloride solution of the complex at -5°C over several days. A single crystal was mounted on a glass fiber with silicon grease and placed into the 123(2) K nitrogen stream of a Siemens R3m/v diffractometer with a modified Enraf-Nonius low-temperature device. Unit cell parameters were determined by least-squares refinement of 26 reflections with $30^\circ < 2\theta < 40^\circ$. The axial lengths and monoclinic crystal system were verified by examination of axial photographs. Check reflections (2, every 198 reflections) showed only random fluctuations ($<2\%$) in intensity throughout the data collection. The data were corrected for Lorentz and polarization effects. Crystal data for this and all other compounds are given in Table 2.

$\text{Au}_2\text{I}_4\text{AuL}_3$. Red parallelepipeds were grown by slow evaporation of a chloroform-*d* solution of the complex at room temperature over 6 weeks. Data collection followed the procedure outlined for $\text{AuI}_2\text{Au}_2\text{L}_3$.

$\text{Au}_3\text{I}_6\text{L}_3\cdot\text{CH}_2\text{Cl}_2$. Deep red needles were formed by cooling a dichloromethane solution of the compound at -78°C for 1 week. A suitable crystal was mounted on a glass fiber. Data collection followed the procedure outlined for $\text{AuI}_2\text{Au}_2\text{L}_3$.

Solution and Structure Refinement. $\text{AuI}_2\text{Au}_2\text{L}_3$. Calculations were performed using SHELXTL V.5.03 software. Tables of neutral atom scattering factors, f' and f'' , and absorption coefficients are from a standard source.²⁵ The positions of all atoms were located via direct methods. The gold, iodine, and oxygen atoms were refined with anisotropic thermal parameters, while the remaining atoms were refined isotropically. In the final model, three hydrogen atoms were placed on each carbon atom of the methyl groups to provide tetrahedral

geometry for these carbon atoms. A riding model was used with the C-H vectors fixed at 0.96 Å and the thermal parameters set at 1.2 times that of the bound carbon atom. The positions of these hydrogen atom positions were not refined, since the structure is dominated by scattering from heavy atoms. For illustrative purposes, the hydrogen atoms are included in the figures. An empirical absorption correction was applied.²⁶ The largest remaining peak in the electron difference map was 0.758 Å from Au(2) and was equivalent to 2.28 e/Å³.

$\text{Au}_2\text{I}_4\text{AuL}_3$. Analogous procedures were used. The gold, iodine, and chlorine atoms were refined anisotropically, while the remaining atoms were refined isotropically. The largest remaining peak in the electron difference map was 0.876 Å from Au(2), and was equivalent to 4.15 e/Å³.

$\text{Au}_3\text{I}_6\text{L}_3\cdot\text{CH}_2\text{Cl}_2$. Analogous procedures were used. The gold, iodine, and chlorine atoms were refined anisotropically, while the remaining atoms were refined isotropically. The largest remaining peak in the electron difference map was 0.717 Å from Au(2) and was equivalent to 3.91 e/Å³.

Acknowledgment. We thank the National Science Foundation (Grants CHE 9321257 and CHE 9610507) for support.

Supporting Information Available: X-ray crystallographic files, in CIF format, for $\text{AuI}_2\text{Au}_2\text{L}_3$, $\text{Au}_2\text{I}_4\text{AuL}_3$, and $\text{Au}_3\text{I}_6\text{L}_3\cdot\text{CH}_2\text{Cl}_2$, are available on the Internet only. Access information is given on any current masthead page.

IC970612T

(25) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992, Vol. C.

(26) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, 28, 53.