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Luminescent Chains Formed from Neutral, Triangular Gold Complexes Sandwiching Tl^I and Ag^I. Structures of $\{Ag([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2\}BF_4\cdot CH_2Cl_2$, $\{Tl([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2\}PF_6\cdot 0.5THF$ (bzim = 1-Benzylimidazolate), and $\{Tl([Au(\mu\text{-}C(OEt){=}NC_6H_4CH_3)]_3)_2\}PF_6\cdot THF$, with MAu_6 ($M = Ag^+, Tl^+$) Cluster Cores

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It has been found that several trinuclear complexes of Au^I interact with silver and thallium salts to intercalate Ag^+ and Tl^+ cations, thereby forming chains. The resulting sandwich clusters center the cations between the planar trinuclear moieties producing structures in which six Au^I atoms interact with each cation in a distorted trigonal prismatic coordination. The resultant $(B_3AB_3B_3AB_3)_\infty$ pattern of metal atoms also shows short (∼3.0 Å) aurophilic interactions between BAB molecular centers. These compounds display a strong visible luminescence, under UV excitation, which is sensitive to temperature and the metal ion interacting with the gold. X-ray crystal structures are reported for $Ag([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2BF_4\cdot CH_2Cl_2$ ($P\bar{1}$, $Z = 2$, $a = 14.4505(1)$Å; $b = 15.098(2)$Å; $c = 15.957(1)$Å; $\alpha = 106.189(3)°$; $\beta = 103.551(5)°$; $\gamma = 101.310(5)°$); $Tl([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2PF_6\cdot 0.5C_4H_8O$ ($P\bar{1}$, $Z = 2$, $a = 15.2093(1)$Å; $b = 15.3931(4)$Å; $c = 16.1599(4)$Å; $\alpha = 106.018(1)°$; $\beta = 101.585(2)°$; $\gamma = 102.068(2)°$); and $Tl([Au(\mu\text{-}C(OEt){=}NC_6H_4CH_3)]_3)_2PF_6\cdot C_4H_8O$ ($P2(1)/n$, $Z = 4$, $a = 16.4136(3)$Å; $b = 27.6277(4)$Å; $c = 16.7182(1)$Å; $\beta = 105.644(1)°$). Each compound shows that the intercalated cation, Ag^+ or Tl^+, coordinates to a distorted trigonal prism of six Au^I atoms. The counteranions reside well apart from the cations between the cluster chains.

Introduction

Over the past two decades, numerous advances have been made in the chemistry of gold.[1] Au^I centers play an important role as supramolecular components yielding infinite structures[2,3] with interesting chemical and physical properties that might be used, for example, in molecular devices.[4−6] Recently, the structure of $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3$ was reported[7,8] as an infinite trigonal column with extensive intermolecular Au- - -Au interactions. This columnar stacking is not present in the related $[Au(\mu\text{-}C(OMe){=}NCH_2C_6H_5)]_3$.[9] The methyl compound $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3$ shows a solvent-stimulated emission, a "solvoluminescence". Moreover, a columnar mesophase of a cyclic Au^I pyrazolate complex has been described.[10] Scheme 1 is a molecular drawing of the various trinuclear complexes used in this study.

Trinuclear cyclic Au^I compounds have been known since 1970 when Vaughan[11] reported the synthesis of organogold complexes of the 2-pyridyl ligands. These compounds were proposed as trinuclear cyclic Au^I species on the basis of the coordination requirements of the Au^I. In the following years, analogous compounds were isolated, and depending on the types of 1,2 bridging ligands, N−Au−C,[12,13] or N−Au−N,[14] various arrangements were described, and some of these have been structurally characterized.[15−17] These structures show nine-atom rings where the intramolecular Au- - -Au distances range from 3.224(1) to 3.368(1) Å indicating weak metal−metal interactions. There also is one example, to date, in which six Au^I atoms

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(1) Schmidbaur, H., Ed. *Gold, Progress in Chemistry, Biochemistry and Technology*; John Wiley & Sons: Chichester, England, 1999.
(2) Schneider, W.; Bauer, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1997**, 415.
(3) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1996,** 561.
(4) Mills, A.; Lepre, A.; Theobald, B. R. C.; Slade, E.; Murrer, B. A. *Gold Bull*. (*London)* **1998**, *31*, 68.
(5) Ma, Y.; Che, C.-M.; Chao, H.-Y.; Zhou, X.; Chan, W.-H.; Shen, J. *Adv. Mater*. **1999**, *11*, 852.
(6) Kunugi, Y.; Mann, K. R.; Miller, L. L.; Exstrom, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 589.
(7) (a) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179. (b) Balch, A. L.; Doonan, D. J. *J. Organomet. Chem.* **1977**, *131*, 137.
(8) Gade, L. H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1171.
(9) Balch, A. L.; Olmstead, M. M.; Vickery, J. C. *Inorg. Chem.* **1999**, *38*, 3494.
(10) Barberà, J.; Elduque, A.; Gimenez, R.; Oro, L. A.; Serrano, J. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2832.
(11) Vaughan, L. G. *J. Am. Chem. Soc.* **1970**, *11*, 730.
(12) Minghetti, G.; Bonati, F. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 429. Minghetti, G.; Bonati, F. *Inorg. Chem.* **1974**, *13*, 1600.
(13) Bonati, F.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1989**, *375*, 147.
(14) Bonati, F.; Minghetti, G.; Banditelli, G. *J. Chem. Soc., Chem. Commun.* **1974**, 88.
(15) Tiripicchio, A.; Tiripicchio Camellini, M.; Minghetti, G. *J. Organomet. Chem.* **1979**, *171*, 399.
(16) Murray, H. H.; Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 26.
(17) Bovio, B.; Bonati, F.; Banditelli, G. *Inorg. Chim. Acta* **1984**, *87*, 25.

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Scheme 1

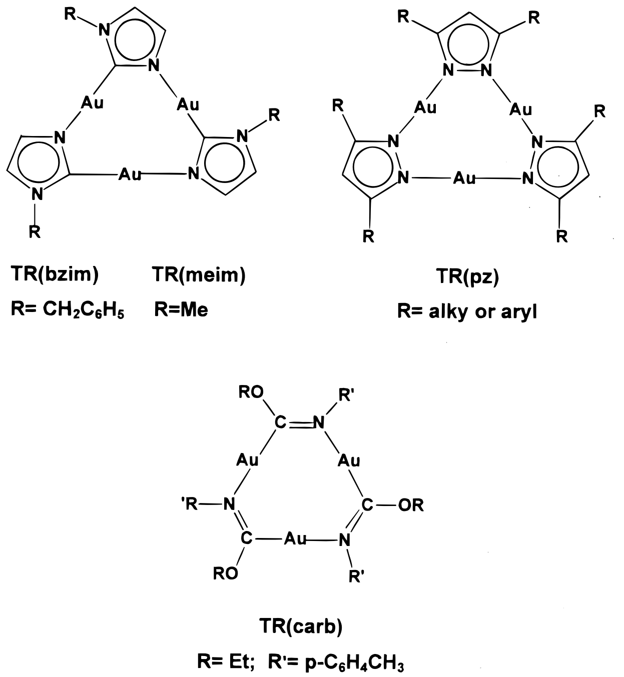

Table 1. List of Compounds[a]

no.	ligand, μ−C,N−L	compound
1	bzim, 1-benzylimidazolate	$\{[TR(bzim)]_2Ag\}BF_4$
2	bzim	$\{[TR(bzim)]_2Ag\}PF_6$
3	meim, 1- methylimidazolate	$\{[TR(meim)]_2Ag\}BF_4$
4	carb, $C(OEt){=}NC_6H_4CH_3$	$\{[TR(carb)]_2Ag\}BF_4$
5	bzim	$\{[TR(bzim)]_2Tl\}PF_6$
6	carb	$\{[TR(carb)]_2Tl\}PF_6$
7	bzim	$\{TR(bzim)Ag\}ClO_4$
8	bzim	$[TR(bzim)][AgClO_4]_2$
9	carb	$\{[TR(carb)]_2Ag\}ClO_4$

[a] See Scheme 1 for structures of the trinuclear Au^I compounds denoted here as TR(bzim), TR(meim), and TR(carb).

form an 18-atom ring: a loop in which two nonadjacent Au^I atoms in the ring approach each other to about 3.5 Å.[18] Hawthorne and colleagues[19] have described related trinuclear and tetranuclear mercury ring (mercuracarborands) compounds.

Reactivity studies of trimeric Au^I complexes of the type described above indicate that the bridging ligands play an important role in the observed chemistry. The carbeniato Au^I derivatives undergo stepwise oxidative halogen additions to form three distinct complexes $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3X_n$ ($n = 2$, 4, 6; X = Br or I).[20] The structures of the oxidized iodine complexes were recently reported.[21] In contrast, the pyrazolate trimers $[Au(\mu\text{-}3,5\text{-}R_2pz)]_3$ (R = alkyl) and $[Au(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pz)]_3$ only oxidize at one center, yielding the mixed-valence Au^I−Au^I−Au^{III} complexes $[Au(\mu\text{-}3,5\text{-}R_2pz)]_3I_2$[22] and $[Au(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pz)]_3Cl_2$,[23] respectively. In addition, $[Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3$ (C^2,N^3-bzim = 1-benzylimidazolate) also undergoes oxidation by only 1 equiv of I_2, yielding the mixed-valence complex $[Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3I_2$.[24] However, this complex can be oxidized completely to an Au^{III} derivative $[Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3Cl_6$ by stronger oxidants such as $SOCl_2$.[25]

Although reactions of $[Ag(PPh_3)_2]^+$ or weakly solvated Ag^+ or $[AuPPh_3]^+$ ions with transition metal clusters represent well-known methods for cluster expansion synthesis,[26−29] only recently has this strategy been used with cyclic trimer Au^I complexes. The structure of the $\{Ag([Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3)_2\}BF_4$ has been described by several of us in a preliminary communication.[30] Related Cu^I, Ag^I, Au^I, Hg^{II}, and Tl^I metal sandwich compounds have been described previously using trinuclear Pt^{II} clusters as the starting material.[31−34] Understanding the bonding interaction of closed-shell metal ions with Au^I in small molecules and clusters has been an experimental and theoretical challenge.[35] Examples containing silver ions have been structurally characterized: $[(F_5C_6)_2Au(\mu\text{-}AgSC_4H_8)_2Au(C_6F_5)_2]_n$,[36] $[(Ph_3PCH_2)_2Au\{\mu\text{-}Ag(OClO_3)_2\}_2Au(CH_2PPh_3)_2]$,[37]and $[Ag(\mu\text{-}dppm)_2\{Au(mes)\}_2]ClO_4$.[38] Recently, Tl^+ and Na^+ have been found to be encrypted by a binuclear Au^I phosphine complex.[39] Vicente and colleagues[40] have coined the term "loose clusters" for these kinds of aggregates of closed-shell d^{10} centers which show unconventional metal−metal interactions or bonds.

Here, we report the syntheses, structures, and preliminary luminescent properties of a new class of sandwich compounds: loose clusters wherein the cations, Ag^+ and Tl^+, are intercalated between electron-rich trinuclear Au^I units. Extended-chain compounds are produced by aurophilic Au^I−Au^I interactions in which four Au^I atoms in each heptanuclear "sandwich" cluster unit interact with two Au^I atoms on each of two neighboring clusters, producing a linear chain $(B_3AB_3B_3AB_3)_n$ pattern.

Results

Trinuclear cyclic Au^I derivatives which have C−Au−N coordination at the Au^I center are electron-rich and react as Lewis bases toward Ag^+ and Tl^+ cations, closed-shell d^{10}, and s^2 metal ion species, respectively, to yield luminescent, heterometallic, "sandwich" clusters. In the preliminary report of the synthesis and structure of the Ag^I complex $\{Ag([Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3)_2\}BF_4$, **1**, it was noted that layering a solution of $AgBF_4$ in MeCN over a CH_2Cl_2 solution of $[Au(\mu\text{-}C^2,N^3\text{-}bzim)]_3$ slowly produced crystals suitable for X-ray crystallographic analysis.

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(18) Raptis, R. G.; Murray, H. H., III; Fackler, J. P., Jr. *J. Chem. Soc., Chem. Commun.* **1987**, *10*, 737.
(19) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267.
(20) Balch, A. L.; Doonan, D. J. *J. Organomet. Chem.* **1977**, *131*, 137.
(21) Vickery, J. C.; Balch, A. L. *Inorg. Chem.* **1997**, *36*, 5978.
(22) Minghetti, G.; Banditelli, G.; Bonati, F. *Inorg. Chem.* **1979**, *18*, 658.
(23) Raptis, R. G.; Fackler, J. P., Jr. *Inorg. Chem.* **1990**, *29*, 5003.
(24) Bovio, B.; Calogero, S.; Wagner, F. E.; Burini, A.; Pietroni, B. R. *J. Organomet. Chem.* **1994**, *470*, 275.
(25) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B. *J. Organomet. Chem.* **1991**, *408*, 271.
(26) Mingos, D. M. P.; Watson, M. J. *Adv. Inorg. Chem.* **1992**, *39*, 327.
(27) Toronto, D. V.; Balch, A. L. *Inorg. Chem.* **1994**, *33*, 6132.
(28) Burrows, A. D.; Gosden, A. A.; Hill, C. M.; Mingos, D. M. P. *J. Organomet. Chem.* **1993**, *452*, 251.
(29) Liu, C. W.; McNeal, C. J.; Fackler, J. P., Jr. *J. Cluster Sci.* **1996**, *7*, 385.
(30) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Pietroni, B. R.; Staples, R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 95.
(31) Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 766.
(32) Hallam, M. F.; Mingos, D. M. P.; Adatia, T.; McPartin, M. *J. Chem. Soc., Dalton Trans.* **1988**, 335.
(33) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329.
(34) Hao, L.; Vittal, J. J.; Puddephatt, R. J. *Inorg. Chem.* **1996**, *35*, 269.
(35) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(36) Uson, R.; Laguna, A.; Laguna, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1097.
(37) Uson, R.; Laguna, A.; Laguna, M.; Uson, A. *Organometallics* **1987**, *6*, 1778.
(38) Contel, M.; Garrido, J.; Gimeno, M. C.; Jimenez, J.; Jones, P. G.; Laguna, A.; Laguna, M. *Inorg. Chim. Acta* **1997**, *254*, 157.
(39) Catalano, V. J.; Bennett, B. L.; Kar, H. M. *J. Am Chem. Soc.* **1999**, *121*, 10235.
(40) Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748.

Table 2. Crystal Data for **$1\cdot CH_2Cl_2$**, **$6\cdot C_4H_8O$**, and **$5\cdot 0.5C_4H_8O$**

chemical formula	$C_{61}H_{56}AgAu_6BCl_{12}F_4N_{12}$ **($1\cdot CH_2Cl_2$)**	$C_{64}H_{80}Au_6F_6N_6O_7PTl$ **($6\cdot C_4H_8O$)**	$C_{62}H_{58}Au_6F_6N_{12}O_{0.50}PTl$ **($5\cdot 0.5C_4H_8O$)**
fw	2404.56	2576.48	2510.34
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
T, K	213(2)	213(2)	213(2)
λ, Å	0.71073	0.71073	0.71073
a, Å	14.4505(1)	16.4136(3)	15.2093(1)
b, Å	15.098(2)	27.6277(4)	15.3931(4)
c, Å	15.957(1)	16.7182(1)	16.1599(4)
α, deg	106.189(3)		106.018(1)
β, deg	103.551(5)	105.644(1)	101.585(2)
γ, deg	101.310(5)		102.068(2)
V, Å^3	3120.3(5)	7300.4(2)	3418.9(1)
Z	2	4	2
ρ_{calcd}, mg/m^3	2.559	2.344	2.438
μ, cm^{-1}	145.05	142.98	152.57
$R1^a$ [$I > 2\sigma(I)$]	0.0572	0.0308	0.0444
wR2^b[$I > 2\sigma(I)$]	0.1004	0.0424	0.0976
$R1^a$ (all data)	0.0894	0.0720	0.0654
wR2^b(all data)	0.1201	0.0465	0.1010

[a] $R1 = \Sigma||F_o| - ||F_c||/|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **$1\cdot CH_2Cl_2$**[a]

Ag(1)−Au(6)	2.731(2)	Au(1)−N(1)	2.02(2)
Ag(1)−Au(3)	2.747(2)	Au(1)−Au(3)#1	3.2678(12)
Ag(1)−Au(5)	2.796(2)	Au(2)−C(1)	1.98(2)
Ag(1)−Au(1)	2.801(2)	Au(2)−N(2)	2.04(2)
Ag(1)−Au(4)	2.866(2)	Au(3)−C(4)	2.01(2)
Ag(1)−Au(2)	2.922(2)	Au(3)−N(3)	2.03(2)
Au(1)−C(7)	2.00(2)	N(1)−C(1)	1.32(3)
Au(6)−Ag(1)−Au(3)	145.13(7)	C(7)−Au(1)−N(1)	173.8(8)
Au(6)−Ag(1)−Au(5)	78.17(5)	C(1)−Au(2)−N(2)	177.2(8)
Au(6)−Ag(1)−Au(1)	115.05(6)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −x, −y−1, −z+1; #2 −x+1, −y−1, −z+1.

Following this scheme with other trinuclear complexes but using THF as the solvent, the following reaction yields the interesting products described here (see Table 1 and Scheme 1):

$$2[\mathrm{Au}(\mu\text{-C,N-L})]_3 + \mathrm{MX} \rightarrow \{\mathrm{M}([\mathrm{Au}(\mu\text{-C,N-L})]_3)_2\mathrm{X}\}$$

When the trinuclear cyclic Au^I complexes TR(pz) (with R = CF$_3$ or Ph) were used as the starting materials, only starting materials were recovered and no reaction was observed. These pyrazolate materials have an N−Au−N coordination.

Each of the clusters **1**−**6** was readily obtained in quantitative or good yield, gave a satisfactory elemental analysis, and produced a colored luminescence when the solid was irradiated by a UV lamp. Successful single-crystal X-ray structural analyses were performed on compounds **1**, **5**, and **6**, the results of which are described here. Table 2 lists the crystallographic information.

Structure of $1\cdot CH_2Cl_2$. Selected bond distances and angles for **$1\cdot CH_2Cl_2$** are listed in Table 3. A thermal ellipsoid plot of the molecular structure of **1** is shown in Figure 1. Figure 2 presents the stacking arrangement that was observed. The molecular structure of the cation of **1** consists of a silver ion bonded to two nine-membered rings of TR(bzim) to form sandwich units. Each Ag^I ion is bonded to six Au^I atoms forming a distorted Ag^I centered trigonal prism of the Au^I atoms with Ag−Au distances ranging from 2.731(2) to 2.922(2) Å, indicative of appreciable metal−metal interaction. These distances are close to those observed in other gold−silver derivatives[34−37,41] wherein the silver atoms bridging two Au^I centers are always supported by other ancillary ligands.

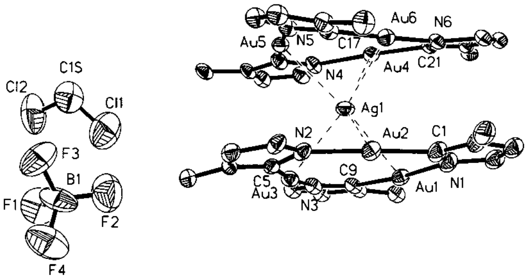

Figure 1. Thermal ellipsoid (50% probability) drawing of the molecular structure of **1**. The benzyl groups are *not* shown.

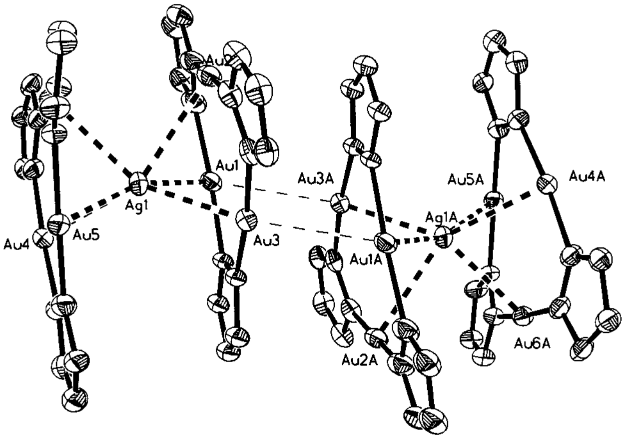

Figure 2. A segment of the chain of **1**. The benzyl groups are *not* shown.

The structure of **1** was the first example in which a naked Ag^I ion is bonded to Au^I atoms, although interesting mixed-metal Au$_x$Ag$_y$ clusters have been known for some time.[42] Recently, another example, [Au$_4$Ag(CH$_2$SiMe$_3$)$_4$(μ-dppm)$_2$]SO$_3$CF$_3$, has been described wherein a naked Ag^I ion is bonded to four Au^I atoms.[43] In this compound the Au−Ag distances range from 2.7179(13) to 2.7822(13) Å. The structural arrangement of the four Au−Ag bonds is similar to the arrangement of the

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(41) Contel, M.; Garrido, J.; Gimeno, C.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1996**, *15*, 4939.

(42) Teo, B. K.; Keating, K. *J. Am. Chem. Soc.* **1984**, *106*, 2224.

(43) Contel, M.; Garrido, J.; Gimeno, M. C.; Laguna, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1083.

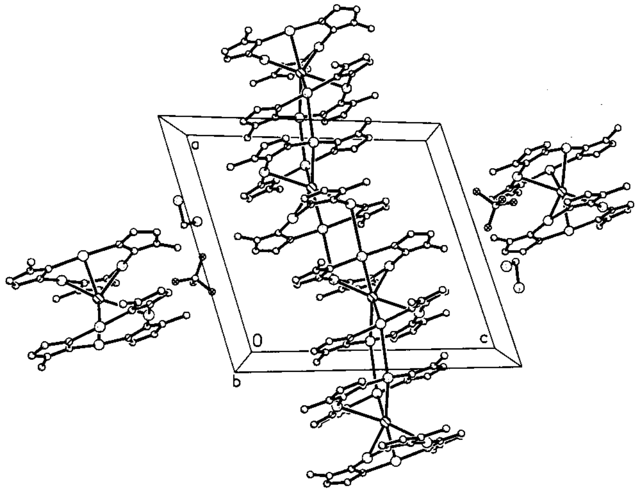

Figure 3. Ball and stick model of the unit cell of **$1 \cdot CH_2Cl_2$** along the *a* axis. Note the core metal atoms joined by lines along this axis.

four Nb−H−M bonds in the niobocene trihydrides,[44] $\{[Nb(C_5H_3RR')_2H_3]_2M\}^+$, M = Cu^I, Ag^I, Au^I. In the cation cluster **1**, the two cyclic moieties of Au^I which form the sandwich units are slightly staggered with respect to each other. The average of Au- - -Au intramolecular distances within each cyclic trimer unit forming the sandwich is 3.19 Å. This distance is shorter than the Au^I- - -Au^I distances observed in $[TR(bzim)]I_2$.[21] Each of the sandwich units interacts with adjacent units with intermolecular aurophilic contacts between four of the Au^I atoms at distances of 3.2678(12) and 3.1157(11) Å. Considering also the positions of the remaining widely separated intermolecular Au^I atoms, a characteristic Au_6 cycle is formed in a "chair" conformation. A similar arrangement has been observed in the structure of the trinuclear carbeniate derivative TR(carb).[13]

The inter- and intramolecular metal−metal interactions observed in **1** result in the formation of an infinite chain of gold and silver atoms, Figure 3, where the $d^{10}-d^{10}$ Ag−Au and Au−Au bonding present can be regarded to arise from correlation and relativistic effects,[45−47] and from charge polarization interactions similar to the cation−π interactions involving aromatic molecules that have been described by Dougherty.[48]

In cluster **1** the bridging imidazolate rings show C−Au and N−Au distances of ca. 2.0 Å, similar to those found in $TR(bzim)I_2$.[21] Three of the N−Au−C angles show significant distortions from linearity, namely N(1)−Au(1)−C(9) [173.9(8)°, N(3)−Au(3)−C(5) [172.9(7)°, and N(6)−Au(6)−C(17) [172.9(7)°. The compound crystallizes with a molecule of the solvent, CH_2Cl_2. The BF_4^- anions are present only as counterions, not interacting in any special way with the Ag−Au cluster.

Structure of 5·0.5THF. Selected bond distances and angles for **5·0.5THF** are listed in Table 4. A thermal ellipsoid drawing of the molecular structure is shown in Figure 6. Figure 7 presents the stacking arrangement that was observed for the clusters. The molecular structure of the Tl^I cluster is nearly identical to the analogous Ag^I sandwich cluster in **1**. The central metal Tl^I atom of the cluster is bonded to six Au^I atoms forming a distorted Tl^I-centered trigonal prism with Tl−Au distances ranging from 2.9711(7) to 3.0448(7) Å. The Au−Tl distances are close to the sum of the metallic radii (3.034 Å) and in the same range found in $[AuTl(Ph_2P(S)CH_2)_2]_n$, 2.959(2)−3.003(2) Å.[49,50] The Au−Tl distances are slightly shorter than the Au−Tl distances, 3.0358(8)−3.0862(8) Å found in $[Tl(OPPh_3)_2][Au(C_6F_5)_2]$,[51] but slightly longer than the distances, 2.9171(5) and 2.9109(5) Å found in $[Au_2Tl(P_2phen)_3])ClO_4)_3$.[39] In contrast to these two examples, the Tl^I in **5** has only the Au^I atoms as nearest neighbors. Tl−Au interactions with long separations, 3.45 Å, also have been found in the luminescent $Tl[Au(CN)_2]$.[52,53]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 5·0.50THF[a]

Tl(1)−Au(6)	2.9711(7)	Au(1)−N(1)	2.061(10)
Tl(1)−Au(1)	2.9905(7)	Au(1)−Au(2)#1	3.1089(7)
Tl(1)−Au(4)	3.0184(7)	Au(2)−C(1)	1.999(12)
Tl(1)−Au(5)	3.0240(7)	Au(2)−N(3)	2.047(9)
Tl(1)−Au(2)	3.0433(7)	Au(3)−C(4)	1.967(13)
Tl(1)−Au(3)	3.0448(7)	Au(3)−N(5)	2.041(10)
Au(1)−C(7)	2.031(12)	N(1)−C(1)	1.349(15)
Au(6)−Tl(1)−Au(1)	149.82(2)	C(1)−Au(2)−N(3)	173.7(5)
Au(6)−Tl(1)−Au(4)	73.247(17)	C(4)−Au(3)−N(5)	176.4(4)
Au(6)−Tl(1)−Au(5)	71.875(17)	C(16)−Au(4)−N(7)	171.5(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+1, −*y*+2, −*z*+1; #2 −*x*+2, −*y*+2, −*z*+1.

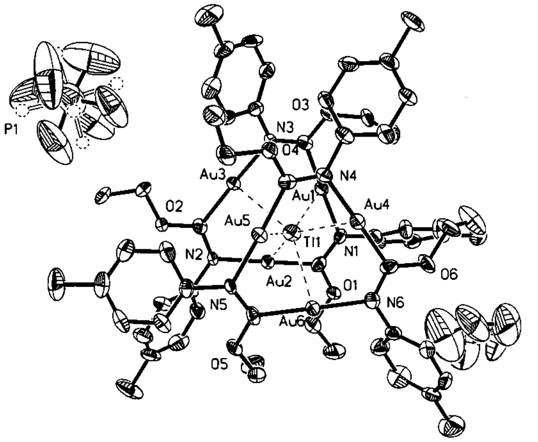

Figure 4. Thermal ellipsoid (50% probability) drawing of the molecular structure of **6·THF**.

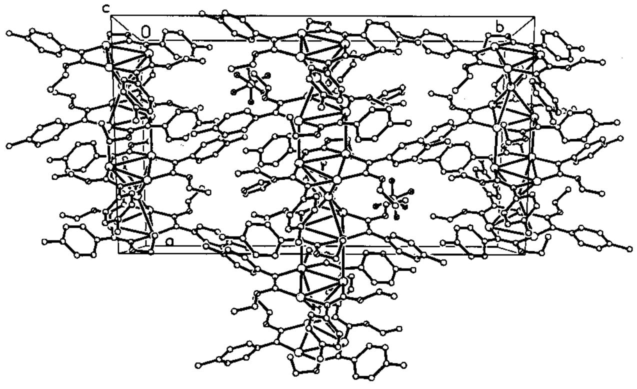

Figure 5. Unit cell of **6·THF**.

The N−Au−C angles of **5** show significant distortions from linearity, ranging from 176.4(4) to 171.5(5)°. These distortions

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(44) Antinolo, A.; Carrillo-Hermosilla, F.; Chaudret, B.; Fajardo, M.; Fernandez-Baeza, J.; Lanfranchi, M.; Limbach, H.; Maurer, M.; Otero, A.; Pellinghelli, M. A. *Inorg. Chem.* **1996**, *35*, 7873.

(45) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

(46) Schmidbaur, H. *Gold Bull. Gold Pat. Dig.* **1990**, *23*, 11.

(47) Kaltsoyannis, N. *J. Chem. Soc., Dalton Trans.* **1997**, 1.

(48) Dougherty, D. A. *Science* **1996**, *271*, 163−68.

(49) Wang, S.; Fackler, J. P., Jr.; King, C.; Wang, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 3308.

(50) Wang, S.; Garzon, G.; King, C.; Wang, J. C.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 4623.

(51) Crespo, O.; Fernandez, E. J.; Jones, P. G.; Laguna, A.; Lopez-de-luzuriaga, M. A.; Monge, M.; Olmos, E. *Chem. Commun.* **1998**, 2233.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 6·THF[a].

Au(1)−C(21)	2.017(7)	Au(3)−C(11)	1.997(6)
Au(1)−N(1)	2.088(5)	Au(3)−N(3)	2.090(5)
Au(1)−Au(3)#1	3.0525(4)	Au(3)−Au(1)#1	3.0525(4)
Au(1)−Tl(1)	3.1031(4)	Au(3)−Tl(1)	3.0970(4)
Au(1)−Au(3)	3.2982(4)	Au(4)−Tl(1)	3.0739(4)
Au(1)−Au(2)	3.3331(4)	Au(4)−Au(6)	3.3133(4)
Au(2)−C(1)	1.983(7)	Au(4)−Au(5)	3.3574(4)
Au(2)−N(2)	2.055(5)	Au(5)−Tl(1)	3.1075(4)
Au(2)−Tl(1)	3.0673(4)	Au(6)−Tl(1)	3.0917(4)
Au(2)−Au(3)	3.3355(4)		
C(21)−Au(1)−N(1)	174.5(2)	Au(2)−Tl(1)−Au(3)	65.516(10)
C(1)−Au(2)−N(2)	176.9(3)	Au(2)−Tl(1)−Au(1)	65.389(9)
Au(1)−Au(2)−Au(3)	59.284(7)	Au(3)−Tl(1)−Au(1)	64.276(9)
C(11)−Au(3)−N(3)	175.0(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*+1, −*y*, −*z*+1; #2 −*x*, −*y*, −*z*+1.

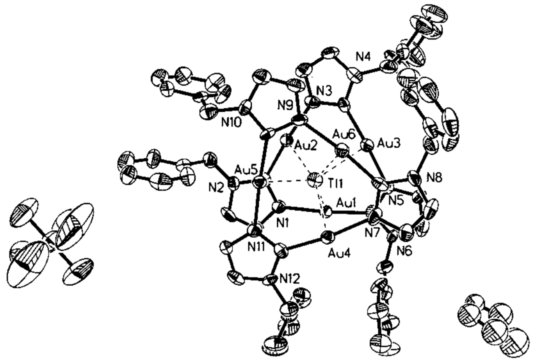
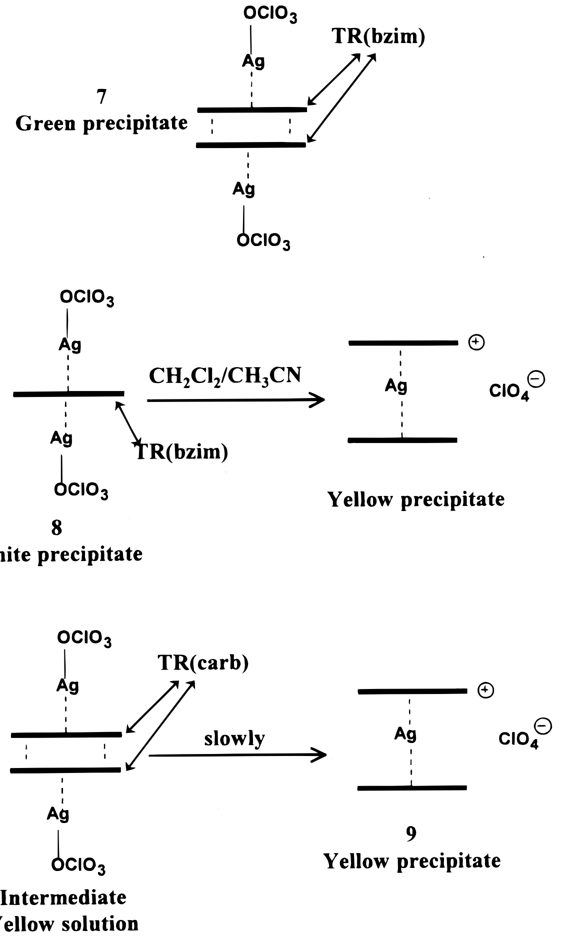


Figure 6. Thermal ellipsoid (50% probability) drawing of the molecular structure of **5·0.5THF**.

are a bit more pronounced than those found in **1** and may reflect a stronger interaction of the Tl^I than the Ag^I with the Au^I atoms. The average intramolecular Au- - -Au distance in the cyclic trimeric moiety forming the sandwich unit is 3.08 Å, a slightly shorter distance than the average distance observed in the analogous Ag^I cluster. As in **1**, two Au^I atoms on each trinuclear unit are involved in intermolecular aurophilic bonding interactions at 3.1089(7) and 3.0658(7) Å, forming infinite chains along the crystallographic *a* axis. The PF_6^- anions sit between the metal chains along with the THF solvent molecules.

Structure of 6·THF. Selected bond distances and angles for **6·THF** are listed in Table 5. A thermal ellipsoid drawing of the molecular structure of **6** is presented in Figure 6. The unit cell with the observed characteristic stacking arrangement is seen in Figure 5. The molecular structure of this Tl^I cluster is similar to the structures of **1** and **5**. However, the bridging ligands which form the cyclic trinuclear Au^I units are the carbeniato ligand $C(OEt){=}NC_6H_4CH_3$. The average C−Au and N−Au distances are 2.005 and 2.067 Å, respectively, which are slightly longer than the average values found in the cyclic Au^I unit TR(carb).[7] The N−Au−C angles of **6** show significant distortions from linearity, as was found in both **1** and **5**. The central Tl^I metal atom of the sandwich unit is bonded to six Au^I atoms as in the other intercalated complexes, forming a distorted, Tl^I-centered trigonal prism of Au^I atoms. The Tl−Au distances range from 3.0673(4) to 3.1075(4) Å. A polymeric chain, Figure 7, is formed by intermolecular, aurophilic bonds at distances of 3.0588(4) and 3.0525 Å. In the crystal of **6**, the disordered PF_6^- anions are found between the chains along with THF.

Scheme 2



Reactions of the Cyclic Trimeric Au^I Compounds with $AgClO_4$. When $AgClO_4$ in THF is reacted with the trimeric cyclic Au^I substrates, several different observations are made. The stoichiometry of the reaction plays an important role. Upon reaction of TR(bzim) with $AgClO_4$ in a 1:1 molar ratio, the product TR(bzim)[$AgClO_4$], **7**, is isolated as a green, luminescent precipitate. Using a 1:2 molar ratio yields a cluster having the formula [TR(bzim)][$AgClO_4$]$_2$, **8**, as a white precipitate. In both clusters the ClO_4^- anion appears, from the IR analysis, to be coordinated to Ag^I (IR: 1095 (s, br); 1048 (m); 918 (w); 622 (w) cm^{-1}). Although crystals suitable for X-ray structural analysis have not been obtained to date, the chemical analyses and the spectral data are consistent with the structures suggested in Scheme 2. Compounds **7** and **8** and the “intermediate” shown in Scheme 2 are likely to be “half-sandwich” species with Au^I−Au^I interactions occurring in the colored 1:1 complex. In **8**, the two faces of a single cyclic trinuclear Au^I compound may be bicapped by two Ag^I perchlorate moieties, with no Au^I−Au^I intermolecular interactions. The color and luminescence of **7** suggest that intermolecular Au−Au interactions are present. When **8** is crystallized from CH_2Cl_2/CH_3CN, the color turns from white to yellow and the IR spectrum shows that the perchlorate anion is no longer coordinated. The elemental analysis for this final product is in agreement with that expected for a sandwich structure similar to the other sandwich structures reported in this paper.

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(52) Assefa, Z.; DeStefano, F.; Garepapaghi, M. A.; Lacasce, J. H., Jr.; Ouellete, S.; Corson, M. R.; Nagle, J. K.; Patterson, H. H. *Inorg. Chem.* **1991**, *30*, 2868.

(53) Blom, N.; Ludi, A.; Burgi, H. B.; Tichy, K. *Acta Crystallogr.* **1984**, *C40*, 1767.

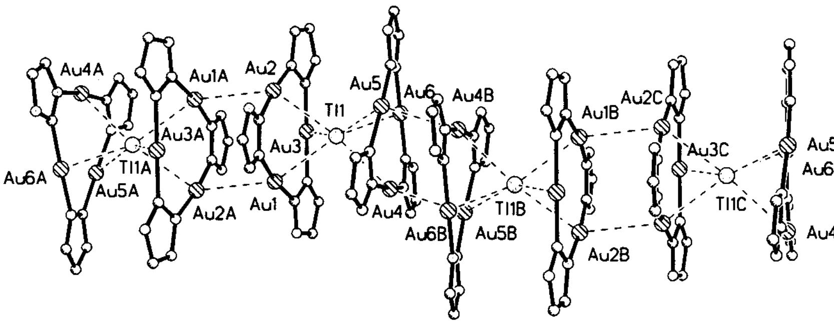

Figure 7. Stacking arrangement of **5·0.5THF**.

When TR(carb) was reacted with $AgClO_4$ in a 1:2 molar ratio, a yellow solution formed immediately (no white precipitate). The reaction was monitored by ^1H NMR in deuterated THF and, with respect to the starting materials, there is a shift in the resonances (see Experimental Section). A bright yellow precipitate, **9**, forms from this solution. The IR spectrum of **9** shows a broad symmetrical peak at 1049 cm^{-1} and a medium peak at 624 cm^{-1}, indicative of uncoordinated ClO_4^-. The elemental analysis and visible luminescence of **9** are in agreement with a sandwich cluster structure similar to the structures obtained crystallographically (Scheme 2). Thus, three different cluster types were isolated using $AgClO_4$ as the silver salt upon reaction with the trinuclear Au^I moieties. The sandwich structure appears to be the most stable material, with products such as **7** and **8** less stable intermediates, insoluble only with the ClO_4^- weakly coordinated to the Ag^+. A white precipitate was observed for a few seconds when cluster **1** was synthesized in a THF solution. It may be a BF_4^- analogue of **8**.

Stability in the Solid State and Behavior in Solution of 1−9. Except for **8**, compounds **1**−**9** appear to be reasonably stable as solids in air at room temperature, although, after several months, some samples produced decomposed material. Improved stability is obtained by storage of the compounds under nitrogen in the dark at 4 °C. Cluster **8** remains white in the presence of the solvent THF, but starts to become pale yellow and decompose when dried under vacuum, probably losing its solvent of crystallization. In general, the clusters having the 1-benzylimidazolate as the bridging ligands bonded to Au^I appear to be more stable than the respective carbeniate derivatives, either in the solid state or in solution.

The Ag^I−Au^I clusters described here are only slightly soluble in the common organic solvents, with the carbeniate derivatives being more soluble than the imidazolates. In coordinating solvents such as DMSO, cluster **1** decomposes to the starting materials. However, using a mixture of a weakly coordinating solvent like acetonitrile and a chlorinated solvent like dichloromethane, crystals of **1** could be obtained. Moreover, in a mixture of deuterated acetonitrile and dichloromethane a ^1H NMR spectrum was recorded for **1**, **5**, and **6**. With respect to the trinuclear cyclic Au^I starting materials, upfield chemical shifts were observed in each case, indicating that these intercalated cation−cluster interactions are present in solution and are not restricted to the solid state materials structurally characterized. The observed upfield shifts were more pronounced for the bzim derivatives, in the range of 0.2−0.3 ppm, than for the carbeniates, where this effect was seen in the range of 0.15 ppm for the ethoxy groups. Some earlier NMR solution studies involving Au^I, such as with $[AuTl(Ph_2P(S)CH_2)_2]_n$ and $[AuPb(Ph_2P(S)CH_2)_4]_n$,[49] have suggested the presence of weak intermolecular interactions.

Luminescence Spectra. Figure 8 shows the luminescence spectra of single crystals of compounds **1**, **5**, and **6**. All three compounds show low-energy visible emissions at ambient temperature (293 K). Interestingly, the three compounds also exhibit *luminescence thermochromism,* as shown by red shifts in the emission maxima which resulted from cooling the crystals to 77 K. For the Ag sandwich compound **1**, the luminescence changes from a green color, $\lambda_{max} \sim 535$ nm, at ambient temperature to an orange glow, $\lambda_{max} \sim 570$ nm, at 77 K (Figure 8a). A similar luminescence color change is observed for the carbeniato Tl sandwich, compound **6**, for which the green luminescence with $\lambda_{max} \sim 525$ nm at ambient temperature becomes orange with $\lambda_{max} \sim 580$ nm (Figure 8b). The bzim Tl sandwich, compound **5**, also shows luminescence thermochromism from a blue emission at ambient temperature to a green emission at 77 K (Figure 8c). Interestingly, the emission profile for **5** is also dependent on the excitation wavelength: at 77 K a strong green emission is observed upon excitation with 420 nm, whereas a yellow emission is seen upon excitation with 475 nm. Preliminary lifetime measurements on the silver complex, **1**, at 298 K, show two different lifetimes of 115 and 550 ns. At lower temperatures, 80−100 K, these lifetimes are 200 and 1100 ns.

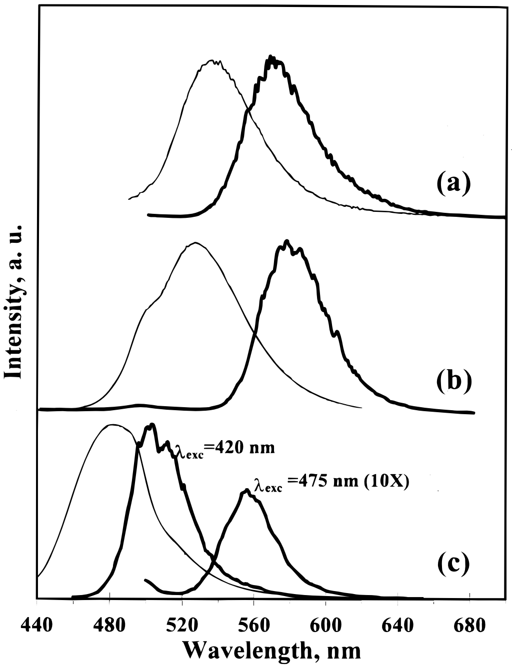

Figure 8. Emission spectra of (a) **1·CH$_2$Cl$_2$**, $Ag[TR(bzim)]_2BF_4$; (b) **6·THF**, $Tl[TR(carb)]_2PF_6$; and (c) **5·0.5THF**, $Tl[TR(bzim)]_2PF_6$; at 293 K (thin line) and 77 K (bold line). Peak intensities have been normalized arbitrarily for the spectra at different temperatures.

Discussion

Although the cyclic trinuclear Au^I complexes TR(bzim), TR(pz), and TR(carb) have been known for many years and have already produced much fascinating new chemistry, their reaction at gold with chemical oxidants has been different for each ligand system. This has suggested an unusual sensitivity to the specific coordination of the gold. Whereas the trinuclear Au^I benzylimidazolate and carbeniate compounds, TR(bzim) and TR(carb) derivatives, respectively, appear to undergo chemical oxidation at all three gold centers by two electrons each (from Au^I to Au^{III}), the pyrazolates studied to date, TR(pz), are oxidized at only one gold center. As reported here, the benzylimidazolate, TR(bzim), and carbeniate TR(carb) compounds with their C−Au−N coordination intercalate Ag^+ and Tl^+ ions into columnar chains to produce new "sandwich" compounds in which six Au^I atoms bond with Ag^+ and Tl^+. Although a columnar chain is known for the sterically unencumbered $[Au(\mu\text{-}C(OMe){=}NCH_3)]_3$, the carbeniate used here, TR(carb), does not have a columnar structure in the solid state, and the structure of the parent TR(bzim) used is unknown. Thus it seems that the cations can induce the formation of a columnar structure even if it is initially absent. Both steric and electronic factors may be involved. Similar products fail to form in our studies with the TR(pz) which has an N−Au−N coordination.

As described in a preliminary communication for **1**, the closed-shell Ag^+ ion bonds with six Au^I atoms of two TR(bzim) units. In addition, these cluster units polymerize into a linear chain $(B_3AB_3B_3AB_3)_n$ pattern by aurophilic Au^I−Au^I bonding between four of the gold atoms of neighboring units. This intermolecular Au−Au distance is 3.268 Å, with two Au^I atoms on each molecular unit having no close intermolecular Au contacts. As listed in Table 1, methylimidazolate and carbeniate compounds of a similar nature also are found to intercalate Ag^+ and Tl^+. The similarity of the thallium structures to those of silver was somewhat surprising at first because the pair of valence electrons on the Tl^+ apparently play no structural role. This had not been the case with $[AuTl(MTP)_2]_n$ where each thallium atom sits in a very distorted tetrahedral $TlAu_2S_2$ geometry, suggesting a structural influence of the 6s electron pair on Tl^+. However, in **5** and **6** the arrangement of the Au^I atoms about Tl^+ is a distorted trigonal prism, which is very similar to the arrangement observed for Ag^+. As with the Ag^I cluster, a polymeric chain is formed in **5** and **6** by short aurophilic Au−Au bonding interactions.

In each of these structures the counteranion sits between chains of clusters, at positions which are well removed from the Tl^+ or Ag^+ cations. Hence, the $[TR(bzim)]_2$ and $[TR(carb)]_2$ units function as bases to the cations, suggesting that the bonding forces between the cations and the neutral gold cluster are largely "ionic". The interactions are reminiscent of the cation−π interactions between aromatic molecules described by Dougherty.[48] Cation−anion Au−Tl interactions have been described by Laguna et al.[38] in an unsupported linear chain of $[Tl(OPPh_3)_2][Au(C_6F_5)_2]$. However, Catalano et al.[39] have recently demonstrated that Au^I is sufficiently basic as a three-coordinate phosphine complex to allow the Au^I to encapsulate Na^+ and Tl^+. We have found that the planar, neutral, trinuclear acid molecule $[Hg(C_6F_4)]_3$ also intercalates into the trinuclear gold clusters chains in a manner similar to the Tl^I and Ag^I, but without counteranions.

The emission spectra of these compounds are interesting and worthy of further study. Low-energy phosphorescence is present consistent with the extended-chain structures observed. The correlation between extended-chain structure and low-energy emission has been indicated in a plethora of studies of group 11 systems. In a recent article, van Zyl et al. have compiled data for a variety of dinuclear gold(I) complexes with phosphor-1,1-dithiolate ligands.[54] A clear correlation has been established between the observation of the low-energy visible emission bands and the existence of extended-chain structure with *inter*molecular Au···Au interactions. The luminescence bands in Figure 8 are likely to be associated with excited states that are delocalized along the crystallographic axis of the chain. Thermal contraction will lead to a reduction in intermolecular metal−metal distances along the chain and reduce the band gap energy. Consequently a red shift of the luminescence is observed when the material is cooled. This trend is well established in extended-chain and layered materials of closed-shell systems, especially for Pt^{II} [55,56] and Au^I.[57,58] Finally, the dependence of the emission profile of **5** on the excitation wavelength indicates the presence of two electronically uncoupled luminescent sites.

Experimental Section

General Procedures. All reactions were carried out under dinitrogen atmosphere and in the dark. Distilled predried solvents were used. $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$, $[Au(\mu\text{-}C^2,N^3\text{-Meim})]_3$ and $[Au(\mu\text{-EtOC}{=}NC_6H_4\text{-}CH_3)]_3$ were prepared as published.[7,12] $AgBF_4$, $AgPF_6$, and $AgClO_4$ were purchased from Aldrich, and $TlPF_6$ was purchased from Strem.

Caution: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and compounds should be handled with great care.*

Elemental analyses were carried out with a Carlo Erba 1106 elemental microanalyzer at Camerino. ^1H NMR spectra were recorded in deuterated solutions on a Varian VXR-300 instrument at 300 MHz or on a Varian Gemini-200 instrument at 200 MHz. Chemical shifts are reported as δ in units of parts per million (ppm). The following abbreviations were used: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quadruplet; m, multiplet; br, broad. Infrared spectra were recorded in the range 4000−200 cm^{-1} on a Perkin-Elmer 1310 spectrophotometer using Nujol mulls in sodium chloride or cesium iodide windows. Excitation and emission spectra were obtained on an SLM/AMINCO model 8100 spectrofluorometer using a 150-W xenon lamp. Low-temperature measurements were made by placing single crystals in a supracell quartz capillary tube, which was inserted into a Dewar flask with a quartz coldfinger. Liquid nitrogen was used to obtain the 77 K data. Preliminary lifetime measurements were made by C. L. Larochelle at the University of Maine using a setup described elsewhere.[52]

Synthesis of $Ag([Au(\mu\text{-}C^2,N^3\text{-bzim})]_3)_2BF_4$, 1·$CH_2Cl_2$. A 30-mg sample of $[(Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ (2.8×10^{-2} mmol) was dissolved in 5 mL of THF. A 2.7-mg aliquot of $AgBF_4$ (1.4×10^{-2} mmol) in 1 mL of THF was added without stirring. A white precipitate that quickly turned to a yellow-green luminescent solid was promptly observed. The suspension was stirred for 0.5 h and centrifuged. The solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 98%. Anal. Calcd for $C_{60}H_{54}N_{12}Au_6AgBF_4{\cdot}CH_2Cl_2$: C, 30.47; H, 2.35; N, 6.99. Found: C, 30.83; H, 2.61; N, 6.65. ^1H NMR (δ in CD_2Cl_2/CD_3CN, 4:1): 7.40−7.20 ppm, m, $-C_6H_5$; 7.01 ppm, s, broad, bzim-ring; 6.59 ppm, s, broad, bzim-ring; 5.08 ppm, s, broad, $-CH_2$.

Crystals of **1** suitable for X-ray structure determination were obtained by the following procedures. A 30-mg sample of $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ (2.8×10^{-2} mmol) was dissolved in 5 mL of CH_2Cl_2. A 2.7-mg sample of $AgBF_4$ (1.4×10^{-2} mmol) in 1 mL of CH_3CN was layered over the

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(54) van Zyl, W. E.; Lopez-de-Luzuriaga, J. M.; Fackler, J. P., Jr. *J. Mol. Struct.* **2000**, 516, 99.

(55) Connick, W. B.; Henling, L. M.; Marsh, R. E.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 6261.

(56) (a) Gliemann, G.; Yersin, H. *Struct. Bonding (Berlin)* **1985**, *62*, 87. (b) Yersin, H.; Gliemann, G. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 539.

(57) Fischer, P.; Ludi, A.; Patterson, H. H.; Hewat, A. W. *Inorg. Chem.* **1994**, *33*, 62.

(58) Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1995**, *34*, 4965.

CH_2Cl_2 solution. A yellow-green luminescent precipitate was promptly observed. After several months, the precipitate, standing in contact with the solvent at 4 °C, was completely transformed into small yellow crystals. Yield was 96%.

When $AgPF_6$ was used instead of $AgBF_4$, an analogous precipitate of **1** formed but with a PF_6^- counteranion. This compound, **2**, was isolated in nearly quantitative yield, and was characterized by elemental analysis. Anal. Calcd for $C_{61}H_{56}N_{12}Cl_2Au_6AgPF_6$: C, 30.44; H, 2.35; N, 6.99. Found: C, 30.02; H, 2.45; N, 6.83.

Synthesis of Ag([Au(μ-C^2,N^3-Meim)]$_3$)$_2$BF$_4$, 3. A 50-mg sample of [Au(μ-C^2,N^3-Meim)]$_3$ (6.0×10^{-2} mmol) was dissolved in 10 mL of THF. A solution containing 5.8 mg of $AgBF_4$ (3.0×10^{-2} mmol) in 2 mL of THF was added without stirring. After the immediate formation of a white-yellow solid, a flaky bright green-yellow precipitate was formed within a few minutes. The suspension was stirred 0.5 h and centrifuged. The solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 51%. Anal. Calcd for $C_{24}H_{30}N_{12}Au_6AgBF_4$: C, 15.47; H, 1.62; N, 9.02. Found: C, 15.99; H, 1.69; N, 9.22.

Synthesis of [Ag{[Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$}$_2$]BF$_4$, 4. A 20-mg sample of [Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$ (1.8×10^{-2} mmol) was dissolved in 4 mL of THF. A solution of 1.8 mg of $AgBF_4$ (0.9×10^{-2} mmol) in 0.5 mL of THF was added without stirring. The immediate formation of a flaky orange precipitate was observed. This suspension was stirred for 0.5 h and centrifuged. The solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 83%. Anal. Calcd for $C_{60}H_{72}N_6O_6Au_6AgBF_4$: C, 30.67; H, 3.09; N, 3.58. Found: C, 29.53; H, 2.75; N, 3.29. ^{1}H NMR (δ in $CDCl_3$): 7.06 ppm, s, $-C_6H_4$; 4.30 ppm, q, $-CH_2O$; 2.32 ppm, s, $-CH_3$ (tolyl); 1.21 ppm, t, $-CH_3$ (ethoxy).

Synthesis of Tl([Au(μ-C^2,N^3-bzim)]$_3$)$_2$PF$_6$, 5·0.50C$_4$H$_8$O. A 40-mg sample of [Au(μ-C^2,N^3-bzim)]$_3$ (3.8×10^{-2} mmol) was dissolved in 8 mL of THF. A solution of 6.7 mg of $TlPF_6$ (1.9×10^{-2} mmol) in 1 mL of THF was added. After 0.5 h of being stirred, the colorless solution was filtered on Celite and concentrated to 4 mL under vacuum. Hexane (10 mL) was layered on the THF solution. After 1 week, small green crystals suitable for X-ray structure determination were grown. Yield was 78%. Anal. Calcd for $C_{62}H_{58}N_{12}O_{0.5}Au_6TlPF_6$: C, 29.64; H, 2.32; N, 6.69. Found: C, 29.48; H, 2.32; N, 6.33. ^{1}H NMR (δ in CD_2Cl_2/CD_3CN, 4:1): 7.60−7.13 ppm, m, $-C_6H_5$; 7.08 ppm, s, bzim-ring; 6.73 ppm, s, bzim-ring; 5.18 ppm, s, $-CH_2$.

Synthesis of Tl{[Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$}$_2$PF$_6$, 6·C$_4$H$_8$O. A 20-mg sample of [Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$ (1.8×10^{-2} mmol) was dissolved in 6 mL of THF. A solution of 3.3 mg of $TlPF_6$ (0.9×10^{-2} mmol) in 0.5 mL of THF was added. After 0.5 h of being stirred, the colorless solution was filtered on Celite and concentrated to 4 mL under vacuum. Hexane (8 mL) was layered on the THF solution. After 2 weeks at 4 °C, thin green needle-shaped crystals were grown. Yield was 70%. Anal. Calcd for $C_{64}H_{80}N_6O_7Au_6TlPF_6$: C, 29.83; H, 3.13; N, 3.26. Found: C, 28.76; H, 2.86; N, 3.21. ^{1}H NMR (δ in CD_2Cl_2/CD_3CN, 4:1): 7.00 ppm, s, $-C_6H_4$; 4.10 ppm, q, $-CH_2O$; 2.27 ppm, s, $-CH_3$(tolyl); 1.05 ppm, t, $-CH_3$(ethoxy).

Synthesis of [Au(μ-C^2,N^3-bzim)]$_3$[AgClO$_4$], 7. A 12-mg sample of [Au(μ-C^2,N^3-bzim)]$_3$ (1.1×10^{-2} mmol) was dissolved in 4 mL of THF. A 2.1-mg aliquot of $AgClO_4$ (0.9×10^{-2} mmol) in 1 mL of THF was added. A green luminescent precipitate was promptly observed. The suspension was stirred for 0.5 h and then centrifuged. The solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 75%. Anal. Calcd for $C_{30}H_{27}N_6Au_3AgClO_4$: C, 28.38; H, 2.14; N, 6.62. Found: C, 28.06; H, 2.25; N, 6.66.

Synthesis of [Au(μ-C^2,N^3-bzim)]$_3$[AgClO$_4$]$_2$, 8. A 10-mg sample of [Au(μ-C^2,N^3-bzim)]$_3$ (0.9×10^{-2} mmol) was dissolved in 4 mL of THF. A 4.2-mg aliquot of $AgClO_4$ (1.8×10^{-2} mmol) in 2 mL of THF was added. Immediately a green precipitate, which turned to white in a few minutes, was observed. The suspension was stirred for 0.5 h and then centrifuged. The solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 62%. Anal. Calcd for $C_{30}H_{27}N_6Au_3Ag_2Cl_2O_8$: C, 24.39; H, 1.84; N, 5.69. Found: C, 23.97; H, 2.09; N, 6.06.

Synthesis of Ag{[Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$}$_2$ClO$_4$, 9. A 17-mg sample of [Au(μ-C(OEt)=NC$_6$H$_4$CH$_3$)]$_3$ (1.6×10^{-2} mmol) was dissolved in 3 mL of THF. A 7.0-mg aliquot of $AgClO_4$ (3.1×10^{-2} mmol) in 1.5 mL of THF was added. Immediately the solution turned yellow. A precipitate was formed by addition of hexane (6 mL) or by leaving the solution at 4 °C. The resulting flaky, bright yellow solid was washed twice with 2 mL of THF and dried in vacuo. Yield was 63%. Anal. Calcd for $C_{60}H_{72}N_6O_{10}Au_6AgCl$: C, 30.51; H, 3.07; N, 3.56. Found: C, 29.79; H, 3.03; N, 3.42. ^{1}H NMR (δ in THF d^8): 7.15 ppm, dd, $-C_6H_4$; 4.28 ppm, q, $-CH_2O$; 2.69 ppm, s, $-CH_3$(tolyl); 1.49 ppm, t, $-CH_3$(ethoxy).

Structure Determinations of 1, 5, and 6 by X-ray Diffraction. Yellow crystals of **1**, **5**, and **6** suitable for X-ray diffraction analyses were mounted on glass fibers using grease. Data were collected at Harvard University using a Siemens (Bruker) SMART charge-coupled device-based (CCD-based) diffractometer equipped with an LT-2 low-temperature apparatus, operating at 213 K. Data for **1·CH$_2$Cl$_2$** were obtained by using ω scans of 0.3° per frame for 60 s, such that a hemisphere was collected. A total of 1271 frames were collected, and the final resolution was 0.90 Å. Data for **5· 0.5C$_4$H$_8$O** were collected by using ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected, and the maximum resolution was 0.85 Å. Data for **6·C$_4$H$_8$O** were recorded in the same manner as for **5·0.5C$_4$H$_8$O,** and the maximum resolution was 0.75 Å. The first 50 frames were re-collected at the end of each data-collection event to monitor for decay. Crystallographic data for **1**, **5**, and **6** are reported in Table 2.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positions, parameters, and bond lengths and angles for compounds **1**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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