J. Am. Chem. Soc. **2000,** *122,* 11264−11265

Supramolecular Chain Assemblies Formed by Interaction of a *π* Molecular Acid Complex of Mercury with *π*-Base Trinuclear Gold Complexes

Alfredo Burini,*,† John P. Fackler, Jr.,*,‡ Rossana Galassi,†
Tiffany A. Grant,‡ Mohammad A. Omary,‡
Manal A. Rawashdeh-Omary,‡ Bianca R. Pietroni,† and
Richard J. Staples§

Dipartimento di Scienze Chimiche dell' Università
via S. Agostino 1, I-62032 Camerino, Italy
Department of Chemistry and Laboratory for Molecular
Structure and Bonding, Texas A&M University
College Station, Texas 77843
Department of Chemistry and Chemical Biology
Harvard University, 12 Oxford Street
Cambridge, Massachusetts 02138

Received July 11, 2000

The trinuclear cyclic Au^{I} compounds [Au(μ-C^{2},N^{3}-bzim)]$_3$ (bzim=1-benzylimidazolate), **1**, and [Au(μ-C,N−C(OEt)=NC$_6$H$_4$-*p*-CH$_3$)]$_3$, **2**, have been shown[1,2] to interact with metal cations such as Ag^{I} and Tl^{I} to form "sandwich" complexes in which six Au^{I} atoms from two trinuclear gold molecules bond to the Ag^{I} or Tl^{I}. Furthermore, the sandwich units stack to form linear chains with intermolecular aurophilic Au^{I}−Au^{I} bonding between four of the six Au^{I} atoms in adjacent units. Without the cations present, the trinuclear Au^{I} complexes of this type generally are not stacked,[3] although one compound, [Au(μ-C(OMe)=NCH$_3$)]$_3$, is known to stack,[4] and **2** exists as a dimer with two aurophilic Au^{I}−Au^{I} bonds.[5] The stacked compound discovered by Balch produces a very unusual photoluminescence called "solvoluminescence" upon contact with solvent.[4]

Since the trinuclear Au^{I} compounds interact with cations in a similar manner to the cation−π interactions studied by Dougherty,[6] and since Hawthorne[7] and others[8] have demonstrated that polynuclear mercury complexes form crown compounds with anions and various organic and aromatic organometallic substrates, it seemed plausible that acid−base stacking might occur between the trinuclear Hg^{II} complex [Hg (μ-C,C−C$_6$F$_4$)]$_3$, **3**, and the trinuclear Au^{I} complexes. Herein we describe the result of this molecular π acid−base chemistry between the bases **1** and **2** and the acid **3**, their optical properties, and our theoretical interpretation of the observations.

The synthesis of the stacked molecular acid−base crystals resulted from the addition of a solution of **1** or **2** in CH$_2$Cl$_2$ to a solution of **3** in CH$_2$Cl$_2$. An immediate formation of a white 1:1 precipitate occurs, which was separated from the solvent by centrifugation.[9] Recrystallization from acetone/hexane affords crystals suitable for X-ray structural determination and spectroscopic studies. The structures of {[Au(μ-C^{3},N^{3}-bzim)]$_3$}$_2$[Hg(C$_6$F$_4$)]$_3$, **4**, and {[Au(μ-C(OEt)=NC$_6$H$_4$-*p*-CH$_3$)]$_3$}$_2$[Hg(C$_6$F$_4$)]$_3$, **5**, are presented in Figure 1, with the pertinent crystallographic data given below.[10]

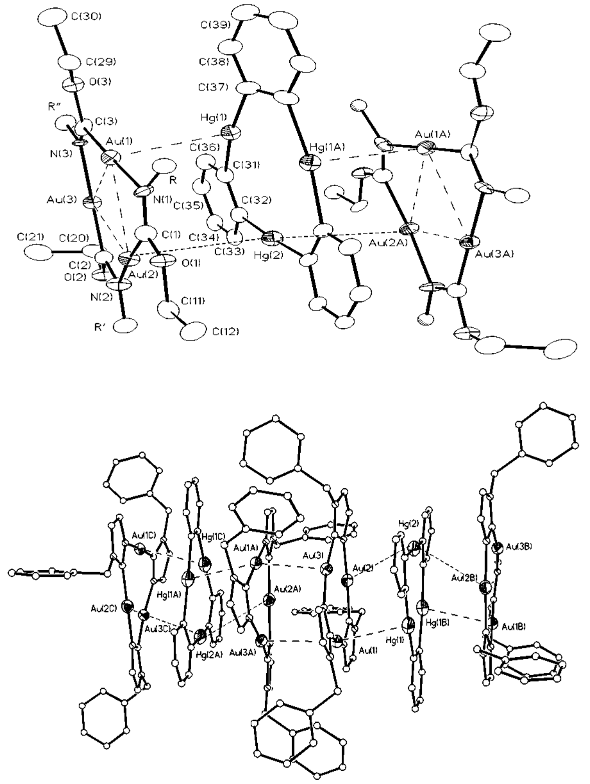

Figure 1. Thermal ellipsoid drawings (40% probability) of the repeating structure of **5** (top) and the extended-chain structure of **4** (bottom). For clarity, the H and F atoms are omitted, and the tolyl groups in **5** are represented by R.

Upon reaction with the trinuclear Hg^{II} complex **3**, the trinuclear Au^{I} complexes **1** and **2** stack, incorporating **3** into the chain, sandwiched between Au^{I} units. This forms an [Au$_3$Hg$_3$Au$_3$]$_n$ repeat pattern with aurophilic interactions. The intermolecular Au···Au distances between the four aurophilically bonded Au^{I} atoms (ca. 3.3−3.5 Å) are typical of those distances found in other Au^{I} complexes having such bonding. The Hg^{II} atoms interact with the Au^{I} atoms in adjacent rings with Hg···Au distances as short as 3.27 and 3.24 Å in **4** and **5**, respectively. Gabbai et al. have observed that benzene produces a 1:1 π stacked complex with **3**, in which each C−C bond in benzene interacts with a different Hg(II) center.[8,11]

---

† Camerino University, Italy.

‡ Texas A&M University.

§ Harvard University.

(1) Burini, A.; Bravi, R., Fackler, J. P., Jr.; Galassi, R., Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* **2000**, *39*, 3158.

(2) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Pietroni, B. R.; Staples, R. J. *J. Chem. Soc., Chem. Commun.* **1998**, 95.

(3) Balch, A. L.; Olmstead, M. M.; Vickery, J. C. *Inorg. Chem.* **1999**, 38, 3494.

(4) (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.

(5) Bovio, B.; Bonati, F.; Banditelli, G. *Inorg. Chim. Acta* **1984**, *87*, 25.

(6) Dougherty, D. A. *Science* **1996**, *271*, 163.

(7) Hawthorne, M. F.; Zheng, Z. *Acc. Chem. Res.* **1997**, *30*, 267.

(8) Gabbaï, F. P.; Schier, A.; Riede, J.; Tschinkl, M. T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3547 and references therein.

(9) Reaction of the trinuclear gold complexes with **3** in a 1:1 or 2:1 molecular ratio affords a white, amorphous product which analyzes as a 1:1 adduct with **2**. Anal. Calcd for C$_{48}$H$_{36}$N$_3$O$_3$Au$_3$Hg$_3$F$_{12}$: C, 27.15; H, 1.71; N, 1.98. Found: C, 27.00; H, 1.48; N, 1.97. Mp: 198−200 °C with decomposition beginning at 186 °C. Crystals suitable for X-ray structure determination were grown from acetone/hexane with the 2:1 composition observed crystallographically. Since it is known that **3** reacts with a variety of organic bases, it is not surprising that a 1:1 adduct forms. The 2:1 product studied crystallographically forms only slowly upon crystallization.

(10) Crystallographic data for **4** and **5** were obtained using a Bruker SMART CCD diffractometer equipped with an LT-2 low-temperature device operating at 213 K. For **4**: orthorhombic, space group *Fddd*, a = 20.1710(4) Å, b = 31.1178(6) Å, c = 61.2451(6) Å, 50 309 data, $R1$ = 0.0481 [$I > 2F(I)$]. Au(1)−C(7), 1.980(13) Å; Au(1)−N(1), 2.028(9) Å; Hg(1)−C(36), 2.103(19) Å; Hg(2)−C(36), 2.103(19) Å; Au−Au$_{\mathrm{intramol,av}}$, 3.456 Å; Au(1)−Au(3)$_{\mathrm{intermol}}$, 3.3298 (5) Å; Au(1)−Hg(1), 3.2749(6) Å; Au(2)−Hg(2), 3.6531 Å. For **5**: monoclinic, space group *C*2/*c*, a = 18.6206(7) Å, b = 22.4385(6) Å, c = 21.1058(7) Å, 23 165 data, $R1$ = 0.0370 [$I > 2F(I)$], β = 112.661(1)°. Au−C$_{\mathrm{av}}$, 1.97 Å; Au−N$_{\mathrm{av}}$, 2.06 Å; Hg−C$_{\mathrm{av}}$, 2.07 Å; Au−Au$_{\mathrm{intramol,av}}$, 3.269 Å; Au(1)−Au(2)$_{\mathrm{intermol}}$, 3.5439 Å; Au(1)−Hg(1), 3.2422 Å; Au(2)−Hg(2), 3.5060(4) Å.

(11) Tsunoda, M.; Gabbaï, F. P. *J. Am. Chem. Soc.* **2000**, *122*, 8335.

10.1021/ja0024690 CCC: $19.00

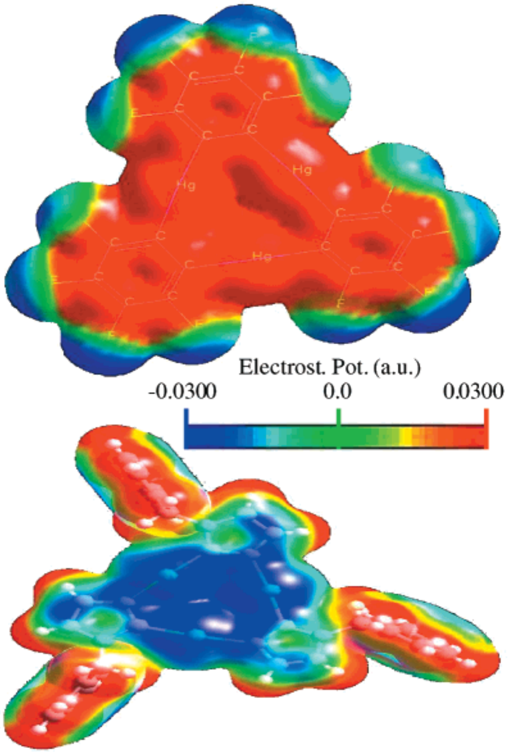

Figure 2. Electrostatic potential values mapped on electron density surfaces of **1** (bottom) and **3** (top) according to DFT calculations.[12]

Figure 2 shows the electrostatic potentials mapped on the electron density surfaces of **1** (bottom) and **3** (top) according to DFT calculations[12] using Gaussian 98.[13,14] The figure clearly shows positive values for the electrostatic potential[12] at the center of the ring of **3**, while negative values are shown at the center of the ring of **1**. Similar figures for the electrostatic potential surfaces in space (not shown) show positive electrostatic potential values above and below the plane of the ring of **3**, while similar regions in **1** have negative values.These results clearly demonstrate the electrostatic nature of the interaction between the mercury ring and the gold rings. DFT calculations for **2** have given qualitative results similar to those described here for **1**.

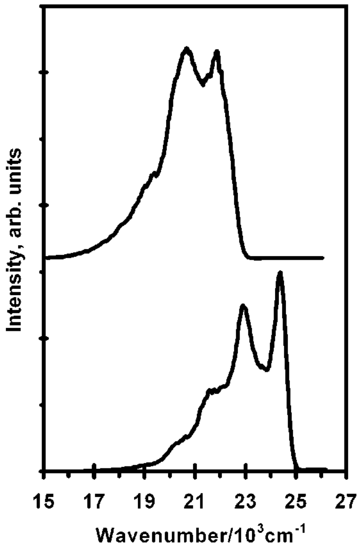

Figure 3. Photoluminescence spectra for crystals of **2** (bottom) and **5** (top) at 77 K.

Crystals of the mixed-metal compounds are luminescent at both ambient and cryogenic temperatures. The emission intensity increases drastically upon Hg−Au interaction. As a representative example, Figure 3 shows the photoluminescence spectra for crystals of **2** and **5** at 77 K. A blue luminescence is observed for **2**. The spectrum shows vibronic structure with an average spacing of ∼(1.4 ± 0.2) × 10^3 cm^{-1}, corresponding to a progression in the $\nu_{C=N}$ vibrational mode of the carbeniate ligand as determined from the infrared spectrum (∼1500 cm^{-1}). This vibronic pattern indicates that the HOMO has a strong C−N ligand character. The presence of well-resolved, structured luminescence has allowed us to determine that the emission and excitation peaks correspond to the 0−1 vibronic transitions, indicating a small Stokes shift and consistent with fluorescence.

Complex **5** exhibits a very strong green luminescence even at ambient temperature, and the spectrum also shows vibronic progression in $\nu_{C=N}$, albeit less resolved than the spectrum for **2**. The formation of the stacked adduct here leads to red shifts in the luminescence excitation and emission peaks by ∼2.8 × 10^3 and 3.7 × 10^3 cm^{-1}, respectively, indicating increased metallophilic bonding in both the ground and excited states. Similar stabilizations have been observed upon interaction of **1** and **2** with Tl^{I} and Ag^{I}.[1]

In conclusion, acid−base interactions between neutral trinuclear complexes of Au^{I} and Hg^{II} lead to the formation of a new class of sandwich complexes. The supramolecular chains formed are stabilized by electrostatic interactions between the Hg_3 and Au_3 units, and by aurophilic bonding between adjacent Au_3 units. The optical properties of the stacked compounds are promising for optoelectronic applications.

Acknowledgment. We thank Lisa M. Thomson for her assistance with the DFT calculations, The Laboratory for Molecular Simulation at Texas A&M University for the computer time, and the Robert A. Welch Foundation and Camerino University for financial support.

Supporting Information Available: X-ray structure reports for **4** and **5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0024690

---

[12] (a) Computational details: All calculations were performed at the density functional theory (DFT) level,[12b] using the Becke three-parameter[12c] hybrid exchange functional and the Lee−Yang−Parr correlation functional (B3LYP).[12d] The Huzinaga/Dunning basis set of double-ζ quality[12e] was used for all atoms except Au, for which the Hay−Wadt effective core potential (ECP) with a double-ζ basis set was used.[12f] Single-point energy and electrostatic potential surface calculations were carried out with geometries taken directly from X-ray crystal structures. (b) Parr, R. G.; Yang, W. *Density-functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Lee, C.; Yang, W; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200. (e) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1976; Vol. 3, p 1. (f) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270; *J. Chem. Phys.* **1985**, *82*, 284; *J. Chem. Phys.* **1985**, *82*, 299.

[13] Frisch, M. J.; Trucks G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.

[14] Graphical representations of the electrostatic potential surfaces were produced using Cerius^2, Release 4.0, Molecular Simulations Inc., 1999.