Chemistry and Optoelectronic Properties of Stacked Supramolecular Entities of Trinuclear Gold(I) Complexes Sandwiching Small Organic Acids

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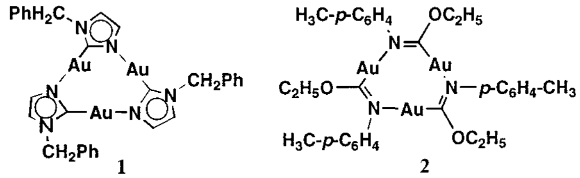
Received May 25, 2001

Extended linear-chain inorganic compounds have special chemical and physical properties.[1,2] This has led to new developments in fields such as supramolecular chemistry, acid−base chemistry, luminescent materials, and various optoelectronic applications. Among the recent examples are the developments of a vapochromic light-emitting diode from linear-chain Pt(II)/Pd(II) complexes,[3] a luminescent switch consisting of an Au(I) dithiocarbamate complex that possesses a luminescent linear-chain form only in the presence of vapors of organic solvents,[4] mixed-metal (Ag/Au) compounds that exhibit different colors and emissions when different organic solvents are introduced or removed,[5] and the discovery of a new phenomenon, solvoluminescence,[6] in a trinuclear Au(I) complex whose extended-chain structure is responsible for storage of energy and release of it as long-lived orange phosphorescence upon contact with solvent.

We have been studying trinuclear Au(I) compounds with aromatic-substituted imidazolate, **1**, and carbeniate, **2**, bridging ligands (Chart 1). These compounds are colorless and do not form extended-chain structures. However, we have recently reported that they can produce brightly colored complexes by sandwiching naked Tl$^+$ and Ag$^+$ ions to form linear-chain complexes with fascinating luminescence properties such as luminescence thermochromism.[7] More recent results have demonstrated that the electron-rich trinuclear Au(I) complexes can interact with the neutral inorganic Lewis acid $Hg_3(\mu\text{-}C_6F_4)_3$ to produce infinite linear-chain complexes.[8] We have then focused our efforts on studying the reactivity of **1** and **2** with small organic Lewis acids and electron acceptors. Balch and co-workers have recently demonstrated that trinuclear Au(I) compounds with alkyl-substituted carbeniate bridging ligands can interact with the large organic acceptors nitro-9-fluorenones.[9] It was suggested that cyano-substituted acceptors should be avoided because the cyanides may directly bind to the "exposed" linear 2-coordinate Au(I) centers.[9] However, DFT calculations that we have carried out[8] clearly show that the donor regions in the trinuclear Au(I) compounds are located at the center of the nine-membered ring and that they extend to regions in space above and below the ring plane, as opposed to being localized on the Au atoms. Indeed, we show here that a charge-transfer complex with a columnar structure does form when a small tetracyano-substituted organic acceptor reacts with **1**. Previous attempts for the reaction with cyano-substituted organic acceptors have lead to the rupture of the trinuclear Au(I) unit and formation of mononuclear cations.[10] We also show here that the liquid organic acid C_6F_6 forms a stacked complex with **2** and quenches its luminescence, thus suggesting a potential sensing action.

Chart 1. Structure of the Trinuclear Compounds Studied



1 **2**

A saturated solution containing 7.0 mg (0.034 mmol) of 7,7,8,8-tetracyanoquinodimethane (TCNQ) dissolved in 1 mL of CH_2Cl_2 was prepared and warmed in a water bath until dissolution. A 35 mg (0.033 mmol) sample of **1** was added to the light-yellow CH_2Cl_2 solution, and an intense green color was observed immediately. Crystallization from CH_2Cl_2/ether produced dark crystals that were analyzed by X-ray crystallography and scanning electron microscopy (SEM).

The product, **3**, of the reaction of **1** with TCNQ was characterized by elemental analysis[11] and X-ray crystallography[12,13] as [**1**]$_2$TCNQ. The crystal structure of **3** is shown in Figure 1. The TCNQ molecule is sandwiched between two units of **1** from each side, in a face-to-face manner so that a molecule of **3** is best represented by the formula (π-**1**)(μ-TCNQ)(π-**1**). The cyanide groups are clearly not coordinated to the gold atoms. The distance between the centroid of TCNQ to the centroid of the Au_3 unit is 3.964 Å. The packing of **3** shows a stacked linear-chain structure, as shown in Figure 1, with a repeat pattern of ···(Au_3)(Au_3)(μ-TCNQ)(Au_3)(Au_3)(μ-TCNQ)··· The stacking in **3** is similar to the previously reported[7,8] sandwich adducts of **1** with Tl$^+$, Ag$^+$, and $Hg_3(\mu\text{-}C_6F_4)_3$, all of which also show a ···BBABBA··· infinite chain pattern with intermolecular aurophilic bonding between four out of the six Au atoms in adjacent Au_3 units. A striking difference in **3**, however, is the two very short intermolecular Au···Au distances of 3.152 Å (identical for the two aurophilic bonds). The intermolecular Au···Au distance in **3** is even shorter than the intramolecular distances in the compound, which were found to be 3.475, 3.471, and 3.534 Å. The adjacent Au_3 units in **3**, as well as in the previously reported adducts of **1** with Tl$^+$, Ag$^+$, and $Hg_3(\mu\text{-}C_6F_4)_3$, form a chair-type structure as opposed to the face-to-face (nearly eclipsed) pattern reported in Balch's studies[9] of the nitro-9-fluorenones adducts with the trinuclear Au(I) alkyl-substituted carbeniate complexes.

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(11) Anal. Calcd (found) for $C_{72}H_{58}N_{16}Au_6$: C, 37.13 (36.60); H, 2.51 (2.34); N, 9.62 (9.25).

(12) Crystallographic data were obtained using a Siemens SMART CCD diffractometer, Mo Kα radiation (λ = 0.71069 Å), T = 110(2) K.

(13) Crystal data for **3**: triclinic, space group *P*-1, a = 11.581(5) Å, b = 11.688(5) Å, c = 13.572(5) Å, α = 106.249(5)°, β = 107.005(5)°, γ = 94.076(5)°, V = 1663.0(12) Å^3, Z = 2, ρ_{calc} = 2.326 g cm^{-3}, 7716 data, R_1 = 0.0579 (all data).

10.1021/ja016279g CCC: $20.00

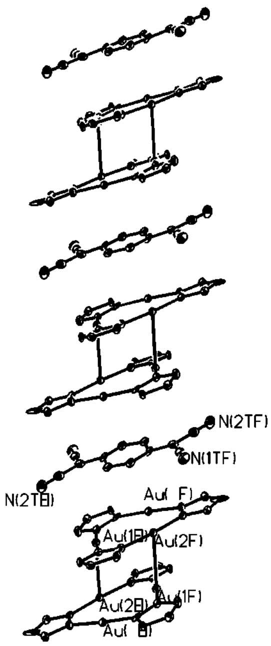

Figure 1. Crystal structure of **3** showing a stereoview of the columnar structure formed by the repeat unit [**1**]$_2$TCNQ. The benzyl groups are omitted for clarity.

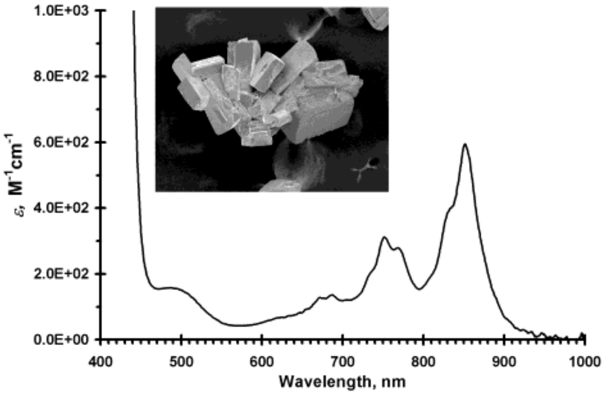

Figure 2. Visible absorption spectrum of **3** in CH_2Cl_2 solution at ambient temperature. The inset shows an SEM image of crystals of **3** taken without coating with a conducting film.

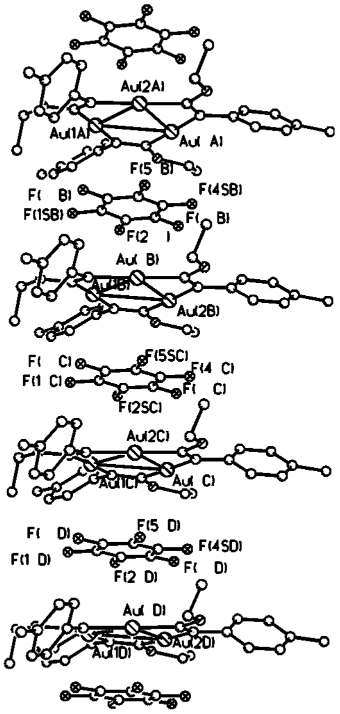

Figure 3. Crystal structure of **4** showing a stereoview of the columnar structure formed by interleaving units of **1** and C_6F_6.

The shortened intermolecular Au−Au distances in **3** may be ascribed to charge-transfer from the electron-rich Au center to the known electron acceptor TCNQ; a partial oxidation of the Au(I) atoms leads to a shortening of Au−Au distances. In the limiting case, upon complete oxidation to Au(II), a gold−gold single bond forms.[14] The charge-transfer assignment is further supported by the dark intense color of **3** (appears black, although thin crystals and films are dark green), in contrast to the colorless crystals of **1** and the light-orange crystals of TCNQ. The color change was the basis of the charge-transfer assignment in ref 9. The charge-transfer adduct forming between **1** and TCNQ is believed to remain intact in solution. Figure 2 shows the absorption spectrum of **3** in a CH_2Cl_2 solution. The spectrum appears to show a small amount of anionic $TCNQ^-$, ε_{max} 43,300 M^{-1} cm^{-1}, when it is compared to absorption peaks below 400 nm for **1** and TCNQ alone. Because its absorption was near 900 nm, it was desired to obtain some data to study the conductivity of **3**. A scanning-electron microscope (SEM) image for crystals of **3** is shown in the inset of Figure 2. The observation of a clear SEM image for crystals of **3** that were not coated with a conducting material suggests that these crystals are noninsulators, because the charge from the electron beam accumulates on the surface of insulating materials, which precludes the observation of a clear SEM image for an insulator.[15] Conducting or semiconducting materials, on the other hand, can diffuse the charge and, thus, allow for the observation of a clear SEM image. We have attempted to carry out preliminary resistivity measurements for a large crystal of **3** that we were able to grow from a saturated CH_2Cl_2 solution containing **1** and TCNQ at 4 °C. However, the resistivity of the crystals at ambient temperature was too high to be measured with the setup we had access to, which can only measure resistivities for conducting materials. The apparent optical band gap of **3** (the absorption edge) is about 1.4 eV, which is within the band gap region for semiconductors, not conductors.

The second adduct we report here was synthesized by suspending a 30 mg sample of **2** (0.028 mmol) in an excess of C_6F_6 (0.1 mL). Methylene chloride was added dropwise and, after each addition, the mixture was stirred and warmed in a water bath until all the solid dissolved. The saturated solution was placed in the refrigerator (4 °C) for crystallization. Colorless single crystals with a high optical purity started to form within a few hours of cooling. The crystals of the product, **4**, were characterized by elemental analysis,[16] X-ray crystallography,[12,17] and photoluminescence spectroscopy. A thermogravimetric analysis for crystals of **4** indicated a weight loss of 14.7% between 73 and 178 °C, corresponding to a loss of one equivalent of C_6F_6 (theoretically 14.8% in **2**·C_6F_6). On melting of **4**, the sample first lost crystallinity at about 160 °C and then decomposed at 180 °C, the exact decomposition point of **2**, which was tested simultaneously.

The crystal structure of **4** shows a columnar stack consisting of alternating C_6F_6 and **2** molecules (Figure 3). The C_6F_6 molecule is sandwiched between two units of **2**, one from each side, in a face-to-face manner so that a molecule of **4** is best represented

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(14) For example, see: (a) Carlson, T. F.; Fackler, J. P. Jr. *J. Organomet. Chem.* **2000**, 596, 237. (b) Yam, V. W. W.; Choi, S. W. K.; Cheung, K. K. *Chem. Commun.* **1996**, 1173.

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(16) Anal. Calcd (found) for $C_{36}H_{36}O_3N_3F_6Au_3$: C, 34.22 (33.90); H, 2.87 (2.72); N, 3.33 (3.30); F, 9.02 (9.08).

(17) Crystal data for **4**: monoclinic, space group $P2_1/c$, $a = 7.3364(12)$ Å, $b = 35.272(6)$ Å, $c = 14.356(2)$ Å, $\beta = 99.804(3)°$, $V = 3660.7(10)$ Å^3, $Z = 4$, $\rho_{calc} = 2.293$ g cm^{-3}, 8978 data, $R_1 = 0.0481$ (all data).

by the formula $(\pi\text{-}\mathbf{2})_{0.5}(\mu\text{-}C_6F_6)(\pi\text{-}\mathbf{2})_{0.5}$. The distance between the centroid of C_6F_6 to the centroid of the Au_3 unit is 3.565 Å. The packing of **4** shows a stacked linear-chain structure (Figure 3) with a repeat pattern of $\cdots(Au_3)(\mu\text{-}C_6F_6)(Au_3)(\mu\text{-}C_6F_6)\cdots$. This is the first example in which the trinuclear Au(I) compounds shown in Chart 1 exist without intermolecular Au−Au aurophilic bonds. The crystal structure of **2** by itself shows a dimeric structure with intermolecular Au−Au bonds.[18] Therefore, the C_6F_6 Lewis acid disrupts the intermolecular aurophilic bonding in **2**, and the resulting linear-chain adduct is stabilized by acid−base interactions. This result is analogous but opposite to the interactions, reported by Gabbaï and co-workers, between the Lewis acid $Hg_3(\mu\text{-}C_6F_4)_3$ and benzene,[19] in which benzene acts as a Lewis base coordinating in a μ-6 manner to six Hg centers, three from each side. The two Au_3 units interacting with hexaflurobenzene in **4** are eclipsed with respect to each other (nearly D_{3h}), whereas the two Hg_3 units in $Hg_3(\mu\text{-}C_6F_4)_3$·benzene[19a] are nearly staggered (D_{3d}).

Crystals of **4** form rather easily in the presence of excess C_6F_6, whereas the trinuclear Au(I) compound **2** by itself is hard to crystallize, and its crystal structure[18] was published several years after the original synthesis of this type of compound was reported.[20] Furthermore, **2** exhibits a blue photoluminescence in the solid state at ambient temperature, whereas the large single crystals of **4** are not luminescent at ambient temperature. We have noticed that when **4** is immersed in a solvent that does not dissolve **2**, such as diethyl ether, the compound loses its crystallinity, and the resulting powder exhibits the blue photoluminescence, characteristic of **2**, indicating that C_6F_6 is liberated from **4**. In contrast, when solid **2** is suspended in C_6F_6, its blue luminescence starts to quench with time. These results have prompted us to study the interaction of these complexes with vapors of organic compounds. Figure 4 shows a representative example from our ongoing investigation in this effort. A solid sample of **2** was placed at a fixed position in a closed chamber, and its luminescence spectra were acquired as a function of time in the presence of C_6F_6 vapors. The vapors were produced as a result of the vapor pressure at ambient temperature (293 K) and pressure (1 atm) of a liquid sample of neat C_6F_6 in a small beaker that is placed at the bottom of the closed chamber. The quenching of the luminescence of **2** was first detected after only several minutes and continued gradually until the next day (Figure 4). A control experiment in the absence of C_6F_6 vapors was carried out and showed no quenching in the luminescence of **2** with time. A detailed photophysical study of changes in the luminescence behavior of **2** and **4** in the presence of a variety of volatile organic molecules will be published elsewhere.

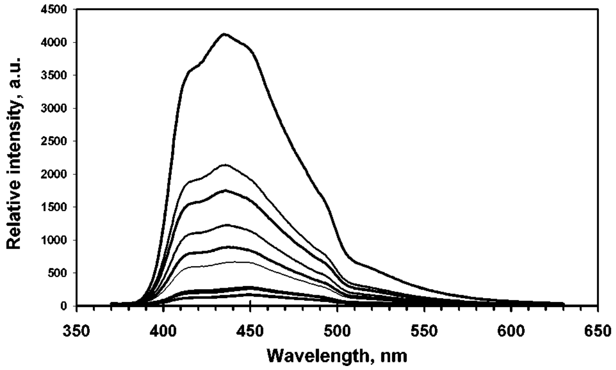

Figure 4. Emission spectra of **2** versus exposure time to C_6F_6 vapor at ambient temperature and pressure. The exposure time was (top-to-bottom) 0, 51, 65, 98, 148, 208, 1322, 1439, and 1462 min, respectively.

The evidence we have gathered thus far suggests that, unlike **3**, **4** dissociates in solution into its component trinuclear Au(I) compound and organic Lewis acid. The electronic absorption spectra for solutions of **4** show the same absorption peaks as those for **2** and C_6F_6. The ^{19}F NMR spectra for even nearly saturated solutions of **4** in $CDCl_3$ show one peak at the same chemical shift (−168 ppm) as that observed for C_6F_6 alone in $CDCl_3$.

In conclusion, this paper reports the interaction of two electron-rich trinuclear gold compounds with two small organic electron acceptors to form acid−base adducts. The resulting compounds have extended-chain structures, which can form regardless of the presence or absence of aurophilic bonds. The benzylimidazolate derivative, **1**, forms a 2:1 charge-transfer complex with the organic electron acceptor TCNQ despite the presence of cyanide groups, which do not coordinate to the Au atoms. The carbeniate derivative, **2**, forms a 1:1 adduct in which the C_6F_6 molecule disrupts the aurophilic bonding that is present in **2** alone. Preliminary results have been presented to illustrate potential optoelectronic applications for the compounds studied, specifically as candidates for new semiconducting materials and sensors for the detection of volatile organic compounds.

Acknowledgment. The financial support of this project has been provided by the Robert A. Welch Foundation of Houston, TX, and the University of Camerino, Italy. The purchase of the CCD X-ray diffractometer was made possible by a Grant from the NSF (CHE-98 07975). We also thank Professors Joel Miller and Kim Dunbar for thoughts about TCNQ.

Supporting Information Available: X-ray crystallographic files for **3** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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