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Alteration of the Aurophilic Interactions in Trimeric Gold(I) Compounds through Charge Transfer. Behavior of Solvoluminescent Au$_3$(MeN=COMe)$_3$ in the Presence of Electron Acceptors

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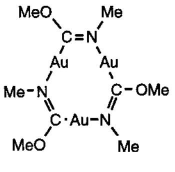
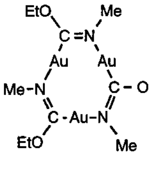
Abstract: The ability of the triangular gold(I) complex, Au$_3$(MeN=COMe)$_3$, which as a solid displays the novel property of solvoluminescence (see: Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179) to function as an electron donor has been demonstrated through spectroscopic studies and isolation of crystalline adducts with organic acceptor molecules. Four such adducts with nitro-9-fluorenones have been isolated and subject to single-crystal X-ray diffraction study. These are deep yellow {Au$_3$(MeN=COMe)$_3$}·{2,4,7-trinitro-9-fluorenone}, red {Au$_3$(MeN=COMe)$_3$}·{2,4,5,7-tetranitro-9-fluorenone}, red {Au$_3$(MeN=COEt)$_3$}$_2$·{2,7-dinitro-9-fluorenone}, and red {Au$_3$(MeN=COEt)$_3$}$_2$·{2,4,7-trinitro-9-fluorenone}. The solid-state structures of {Au$_3$(MeN=COMe)$_3$}·{2,4,7-trinitro-9-fluorenone} and {Au$_3$(MeN=COMe)$_3$}·{2,4,5,7-tetranitro-9-fluorenone} consist of columns in which the planar gold(I) trimers and the nearly planar nitro-9-fluorenones are interleaved with the gold trimers making face-to-face contact with the nitroaromatic portion of the electron acceptor. Thus the organic acceptors disrupt the aurophilic interactions present in crystalline {Au$_3$(MeN=COMe)$_3$} itself. However, in {Au$_3$(MeN=COEt)$_3$}$_2$·{2,7-dinitro-9-fluorenone} and {Au$_3$(MeN=COEt)$_3$}$_2$·{2,4,7-trinitro-9-fluorenone}, aurophilic interactions are found which produce dimers, {Au$_3$(MeN=COEt)$_3$}$_2$, with nearly trigonal prismatic Au$_6$ cores. These dimers are interleaved with the nitro-9-fluorenone molecules to again form extended columns in which the components make face-to-face contact. Despite the fact that the gold atoms in {Au$_3$(MeN=COMe)$_3$} and {Au$_3$(MeN=COEt)$_3$} are in exposed sites and only two-coordinate, there is no evidence of additional coordination of the nitro-9-fluorenones with gold centers in the crystalline adducts.

Introduction

The crystalline gold trimer, {Au$_3$(MeN=COMe)$_3$},[1] displays a novel physical property, solvoluminescence.[2,3] After irradiation with near-UV light, crystals of {Au$_3$(MeN=COMe)$_3$} show a long-lived yellow photoluminescence that is readily detected in a dark room by the human eye for tens of seconds after irradiation ceases. Addition of dichloromethane or chloroform to such previously irradiated crystals produces a bright burst of yellow light. Since the intensity of this emission is greatest for those liquids that are good solvents for {Au$_3$(MeN=COMe)$_3$}, the phenomenon has been termed solvoluminescence. The light produced by solvoluminescence has been shown to correlate with the emission characteristics of the solid rather than those of the molecule in solution. Consequently, the solid-state structure of {Au$_3$(MeN=COMe)$_3$} is crucial to the occurrence of solvoluminescence.


{Au$_3$(MeN=COMe)$_3$}


{Au$_3$(MeN=COEt)$_3$}

Attractive interactions between closed shell Au(I) centers are important in determining the solid-state structures of many gold(I) complexes[4,5] and contribute to the properties of such complexes in solution as well.[6−8] Thus, in the solid state, two-coordinate Au(I) complexes experience attractive aurophilic interactions if the Au···Au separations are less than 3.6 Å.[9−11] Theoretical studies have shown that this weakly bonding interaction is the result of correlation effects which are enhanced by relativistic effects.[12−15] Experimental studies of rotational barriers have shown that the strength of this attractive interaction is comparable to hydrogen bonding: i.e. ca. 7−11 kcal/mol.[5,6] Such aurophilic interactions have been shown to be sufficiently strong to persist in solution and to play a role in guiding a chemical reaction.[8]

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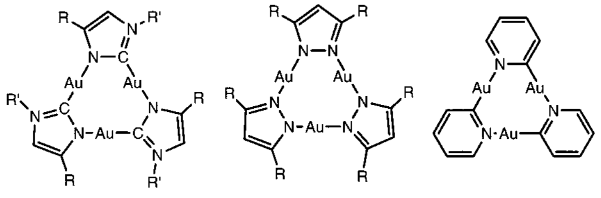
Chart 1



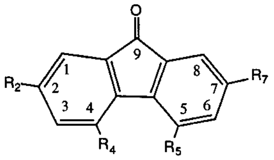
1 **2** **3**

Colorless {Au_3(MeN=COMe)$_3$} crystallizes in the hexagonal space group *P*6/*m* where the individual, flat molecules aggregate along the *c* axis to form columnar stacks. In these stacks the three gold atoms of one molecule lie directly above and below neighboring molecules to form a trigonal prismatic array. The intermolecular $Au^I\cdots Au^I$ distance, 3.346(1) Å, is shorter than 3.6 Å, and an attractive interaction between gold centers is present within the columns. Within each molecule similarly close contacts with an $Au^I\cdots Au^I$ separation of 3.308(2) Å are present. Nevertheless, the C−Au−N angles are all 180°, and there is no evidence that these interactions distort the molecular structure. The other distances and angles within the molecule follow normal expectations. In addition to these ordered stacks, there are other parallel stacks in which there are two sets of positions (one offset by 60° from the other) for the gold triangles. Within the crystal there are two ordered stacks for every disordered stack.

The energy storage required for solvoluminescence of {Au_3(MeN=COMe)$_3$} is likely to involve charge separation within the crystalline solid. This charge separation implies oxidation and reduction of the gold complexes, and it may be facilitated by the mobility of electrons through the $Au^I\cdots Au^I\cdots Au^I$ interactions within the columnar structures found in crystals of {Au_3(MeN=COMe)$_3$}. Consequently, the behavior of {Au_3(MeN=COMe)$_3$} and related complexes toward a range of potential oxidants and reductants is under investigation in this laboratory. Preliminary studies show that {Au_3(MeN=COMe)$_3$} undergoes electrocrystallization to form long, fine needles upon oxidation.[16] Additionally, {Au_3(MeN=COMe)$_3$} undergoes oxidative addition of halogens ($X_2 = I_2$ or Br_2) to form the mixed valence Au(I)/Au(III) complexes, {$Au^I_2Au^{III}X_2$(MeN=COMe)$_3$} and {$Au^IAu^{III}_2X_4$(MeN=COMe)$_3$}, as well as the Au(III) trimer, {$Au^{III}_3X_6$(MeN=COMe)$_3$}.[17,18] These compounds have been isolated in pure form, and characterized both spectroscopically and by single-crystal X-ray diffraction for the iodide adducts. The out-of-plane position of the iodide ligands in these adducts provides an impediment to aurophilic interactions and none are found in these oxidation products.

There are several other trimeric gold(I) complexes that are closely related to {Au_3(MeN=COMe)$_3$}. Relevant examples of these trimeric complexes, which have been studied by Vaughn, Bonati, Fackler, and others, are shown in Chart 1.[19−24] These complexes all involve linear, two-coordinated gold centers connected by bridging ligands to form nearly planar and strain-free, nine-membered rings. While these trimers can pack in the solid state with some degree of Au(I)⋯Au(I) interactions, none have been found to display the prismatic stacking with extended Au(I)⋯Au(I) interactions that is characteristic of {Au_3(MeN=COMe)$_3$}. In addition to examining the oxidative behavior of complexes of the type **2** in Chart 1, Fackler and co-workers have discovered that Ag(I) and Tl(I) can form adducts in which an Ag(I) or Tl(I) ion is bound between two molecules of **2** with close Ag⋯Au or Tl⋯Au contacts.[25,26] Moreover, these Au_3MAu_3 units crystallize into extended chains with M⋯Au(I) and aurophilic Au(I)⋯Au(I) interactions occurring along the chains.

Chart 2



R_2, = NO_2, R_7, R_4, R_5 = H: 2-nitro-9-fluorenone

R_2, R_7 = NO_2, R_4, R_5 = H: 2,7-dinitro-9-fluorenone

R_2,R_4,R_7 = NO_2, R_5 = H: 2,4,7-trinitro-9-fluorenone

R_2,R_4,R_5,R_7 = NO_2: 2,4,5,7-tetranitro-9-fluorenone

Here we report results of the study of the interaction of {Au_3(MeN=COMe)$_3$} and of its closely related analogue, {Au_3(MeN=COEt)$_3$}, with organic acceptors. Since the gold ions within these trimers are only two-coordinate and relatively exposed to direct binding of potential ligands, organic acceptors without coordination were needed. Consequently, the strong acceptors, tetracyanoethylene and quinone based oxidants such as *o*-chloranil, which can directly bind to metal sites, were avoided. For organic acceptors we chose the set of four nitrofluorenones shown in Chart 2. These are all nearly planar molecules with varying acceptor properties. Moreover, they lack likely coordinating sites. Studies of the electrochemical behavior of this group of accepts show, as expected, that the electron accepting ability increases as more nitro groups are present in the molecule.[27] Thus, the half-wave potentials for electrochemical reduction of these nitrofluorenones (with a Ag/AgCl reference electrode) change in the following order: −0.68 V for 2,7-dinitro-9-fluorenone, −0.42 V for 2,4,7-trinitro-9-fluorenone, and +0.14 V for 2,4,5,7-tetranitro-9-fluorenone. Thus 2,4,5,7-tetranitro-9-fluorenone is a slightly weaker electron acceptor than 7,7,8,8-tetracyanoquinodimethane (TCNQ), which has its first one-electron reduction at + 0.29 V, and 2,4,7-trinitro-9-fluorenone is a significantly weaker electron acceptor than tetracyanoethylene, which has a one-electron reduction potential of −0.05 V.[27] The electron accepting properties of these nitrofluorenones are well-known and widely used. For example, nitrofluorenones have been utilized in creating supramolecular structures,[28] in separation of polynuclear aromatic hydrocarbons,[29] in developing electrochromic films,[30] in the formation of photoconducting polymers,[31] and in charge trapping in organic photoconductors.[32] The structures of the crystalline charge-transfer adducts which form are analyzed.

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Table 1. Structural Parameters for Gold Trimers

	$\{Au_3(MeN{=}COMe)_3\}\cdot$ {2,4,7-trinitro-9-fluorenone} (**1**)	$\{Au_3(MeN{=}COMe)_3\}\cdot$ {2,4,5,7-tetranitro-9-fluorenone} (**2**)	$\{Au_3(MeN{=}COEt)_3\}_2\cdot$ {2,7-dinitro-9-fluorenone} (**3**)	$\{Au_3(MeN{=}COEt)_3\}_2\cdot$ {2,4,7-trinitro-9-fluorenone} (**4**)	$\{Au_3(MeN{=}COMe)_3\}^a$ (**5**)
distances (Å)					
Au−C	1.994(6)	2.003(14)	2.015(18)	1.996(17)	2.00(1)
	1.997(5)	2.010(12)	2.004(15)	1.99(2)	
	1.980(6)	1.982(16)	2.022(18)	2.004(17)	
			1.995(15)		
			1.99(2)		
			2.002(16)		
Au−N	2.054(5)	1.962(10)	2.043(15)	2.051(14)	2.03(1)
	2.057(4)	2.043(11)	2.067(15)	2.076(14)	
	2.039(5)	2.032(11)	2.060(14)	2.089(14)	
			2.067(15)		
			2.046(16)		
			2.060(13)		
N═C	1.287(8)	1.268(16)	1.28(2)	1.29(2)	1.29(2)
	1.306(8)	1.280(16)	1.31(2)	1.33(2)	
	1.309(7)	1.327(18)	1.31(2)	1.26(2)	
			1.29(2)		
			1.32(2)		
			1.32(2)		
Au···Au (intra)	3.3214	3.3236(8)	3.2742(10)	3.2910(9)	3.308(2)
	3.3389	3.31409(9)	3.3144(9)	3.3387(9)	
	3.3234	3.3176(9)	3.3710(9)	3.3175(11)	
			3.3176(9)		
			3.3118(10)		
			3.3377(10)		
Au···Au (inter)			3.2438(10)	3.2200(11)	3.346(1)
			3.2328(9)	3.2312(14)	
			3.3545(9)	3.2200(11)	
angles (deg)					
C−Au−N	179.9(2)	175.8(6)	175.7(7)	177.5(6)	180.0(6)
	179.1(2)	176.7(5)	178.0(6)	177.0(6)	
	178.2(2)	176.1(6)	176.5(6)	175.3(6)	
			177.0(7)		
			177.6(8)		
			177.4(7)		

[a] Data from: Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179.

Results and Discussion

Synthetic Studies. The preparation of $\{Au_3(MeN{=}COEt)_3\}$ followed the route devised previously for $\{Au_3(MeN{=}COMe)_3\}$[1] except that the reaction was conducted in ethanol rather than methanol. Colorless needles of $\{Au_3(MeN{=}COEt)_3\}$ were obtained by evaporation of a solution of the complex in diethyl ether. These crystals display a blue luminescence at room temperature when irradiated with a hand-held UV lamp, but they do not display solvoluminescence. Unfortunately, suitable crystals of for a single-crystal X-ray diffraction study of $\{Au_3(MeN{=}COEt)_3\}$ itself were not obtained after repeated attempts. Crystalline charge-transfer adducts of $\{Au_3(MeN{=}COMe)_3\}$ and $\{Au_3(MeN{=}COEt)_3\}$ with the nitro-fluorenones shown in Chart 2 were obtained by mixing the components as dichloromethane solutions followed by either evaporation or the addition of diethyl ether or ethanol. Many other attempts were made to obtain these and other adducts, but only the successful attempts are documented here.

Structural Characterization by X-ray Diffraction. (a) $\{Au_3(MeN{=}COMe)_3\}\cdot$ {2, 4, 7-trinitro-9-fluorenone}, 1. The yellow solid contains one molecule of $\{Au_3(MeN{=}COMe)_3\}$ and one of 2,4,7-trinitro-9-fluorenone in the asymmetric unit with no crystallographically imposed symmetry for either molecule. Table 1 presents interatomic distances and angles for the gold trimers in this and other relevant compounds. The internal structure of the gold trimer is similar to that found earlier for $\{Au_3(MeN{=}COMe)_3\}$ itself.[2] Similarly, the structure of the fluorenone portion is structurally like that found previously for pristine 2,4,7-trinitro-9-fluorenone.[33] Figure 1 shows a drawing of both molecules from a vantage point that looks perpendicular to the Au_3 plane within the gold trimer and thus shows how the two molecules overlap one another. As seen here the three gold atoms of a trimer lie over and nearly parallel to the aromatic ring of the 2,4,7-trinitro-9-fluorenone molecule that contains the two nitro groups. In this view the closest contacts between gold centers of the trimer and carbon atoms of the organic acceptor are as follows: Au(1)···C(14), 3.374 Å; Au(2)···C(12), 3.422 Å; Au(3)···C(16), 3.326 Å, and Au(3)···C(17), 3.589 Å. Figure 2 shows how the individual molecules of the gold trimer and of 2,4,7-trinitro-9-fluorenone are interleaved to form columns within the crystal. The column is formed by simple repeat of one of the gold trimers and one 2,4,7-trinitro-9-fluorenone molecule along the *b* axis ($b = 6.7133(3)$ Å). These columns are tilted by 7.8° from the normal to the Au_3 planes within the gold trimers. On the opposite side of the gold trimer from that shown in Figure 2, the closest gold carbon contacts are as follows: Au(1)···C(14A), 3.365 Å; Au(2)···C(12A), 3.449 Å; Au(2)···C(16A), 3.559 Å; and Au(3)···C(17A), 3.401 Å.

(b) $\{Au_3(MeN{=}COMe)_3\}\cdot$ {2,4,5,7-tetranitro-9-fluorenone}, 2. The asymmetric unit of this red solid contains two molecules

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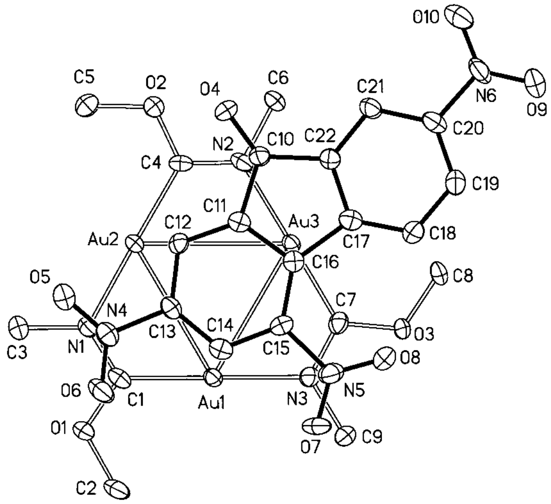

Figure 1. A projection of a 2,4,7-trinitro-9-fluorenone molecule onto the Au$_3$ plane of {Au$_3$(MeN═COMe)$_3$} in {Au$_3$(MeN═COMe)$_3$}·{2, 4, 7-trinitro-9-fluorenone}, **1**, with 50% thermal contours for all non-hydrogen atoms. The hydrogen atom positions are not shown.

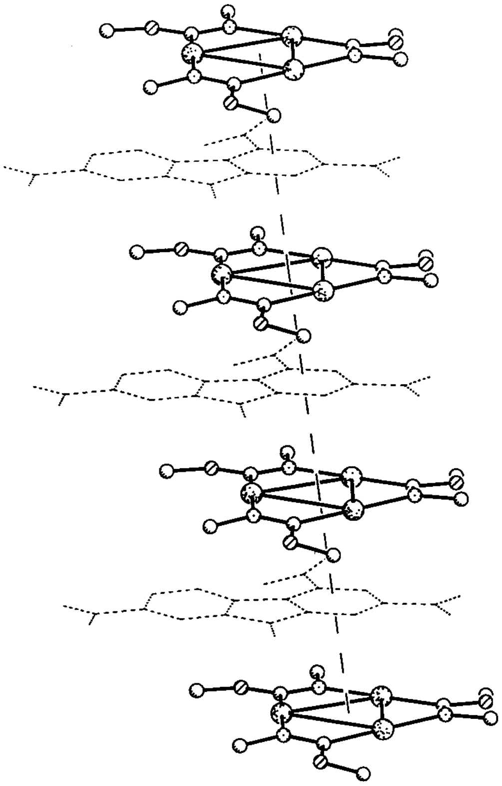

Figure 2. A view of the column formed by the interleaving of gold trimers and nitrofluorenone molecules in crystalline {Au$_3$(MeN═COMe)$_3$}·{2,4,7-trinitro-9-fluorenone}, **1**.

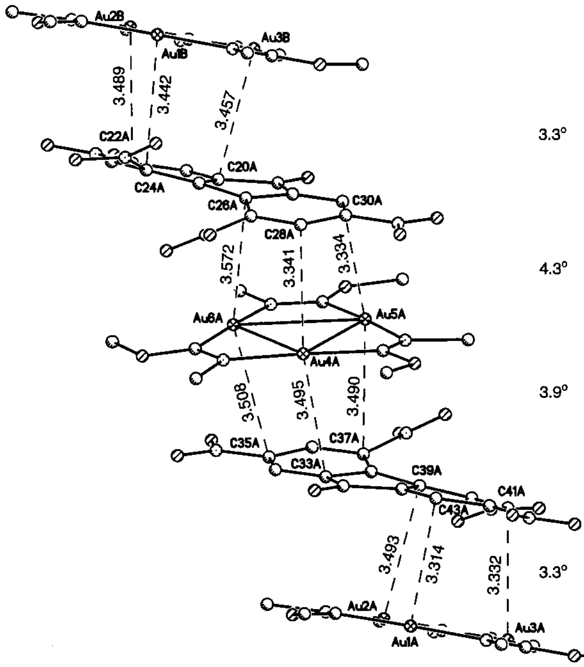

Figure 3. A view of the column formed by the interleaving of gold trimers and nitrofluorenone molecules in crystalline {Au$_3$(MeN═COMe)$_3$}·{2,4,5,7-tetranitro-9-fluorenone}, **2**. Distances are given in Å.

of {Au$_3$(MeN═COMe)$_3$} and two molecules of 2,4,5,7-tetranitro-9-fluorenone in the asymmetric unit with no crystallographically imposed symmetry for any of the molecules. Again the structures of the individual molecules are analogous to those found for the individual components, {Au$_3$(MeN═COMe)$_3$}[2] and 2,4,5,7-tetranitro-9-fluorenone.[34,35] Figure 3 shows a drawing of the structure (with {Au$_3$(MeN═COMe)$_3$} molecules at the major site, see below) that emphasizes how the different molecules are arranged. As with {Au$_3$(MeN═COMe)$_3$}·{2,4,7-trinitro-9-fluorenone}, the molecules in {Au$_3$(MeN═COMe)$_3$}·{2,4,5,7-tetranitro-9-fluorenone} form interleaved stacks in which the two different molecules alternate. Each molecule of {Au$_3$(MeN═COMe)$_3$} makes face-to-face contact with two different molecules of 2,4,5,7-tetranitro-9-fluorenone, and each molecule of 2,4,5,7-tetranitro-9-fluorenone makes face-to-face contact with two different molecules of {Au$_3$(MeN═COMe)$_3$}. Each face of a gold trimer is positioned above or below one of the dinitrophenyl rings of the 2,4,5,7-tetranitro-9-fluorenone molecules that surround it. The spacings between the individual molecules, as measured by the shortest intermolecular Au···C distances, are shown in Figure 3. These spacings are similar to what is seen in {Au$_3$(MeN═COMe)$_3$}·{2,4,7-trinitro-9-fluorenone}.

However, the organization of the stacks in {Au$_3$(MeN═COMe)$_3$}·{2,4,5,7-tetranitro-9-fluorenone} is more complex because of the presence of four independent molecules in the stack and the fact that the molecules of 2,4,5,7-tetranitro-9-fluorenone are distorted from planarity. The nonplanarity of the 2,4,5,7-tetranitro-9-fluorenone molecules is caused by the need to avoid contact between the nitro groups in the 4 and 5 positions. To minimize this contact, the carbon skeleton of the fluorenone molecules is twisted and the nitro groups themselves are turned so that they are no longer coplanar with the aromatic core. The dihedral angles between the NO$_2$ groups and the mean plane of the C$_6$ ring to which they are attached fall into two groups. For the nitro groups in the 2 and 7 positions these angles are small (1.3° for N(7), 3.1° for N(9), 3.6° for N(11), and 4.6° for N(13)) and the groups approach coplanarity. However, for the nitro groups in the 4 and 5 positions the dihedral angles are larger (31.3° for N(8), 28.6° for N(10), 31.7° for N(12), and 25.2° for N(14)) as a result of the need to avoid contact with one another. These distortions of the fluorenone skeleton and of the nitro groups are also present in crystals of 2,4,5,7-tetranitro-9-fluorenone itself.[34,35] Again the dihedral angles between the NO$_2$ groups and the C$_6$ ring fall into two groups: smaller angles (7.5, 14.1, 14.8, 16.4°) for the nitro groups in

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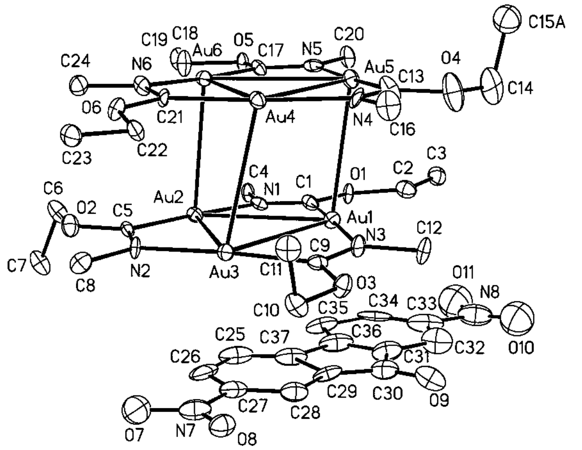

Figure 4. A view of the components of {Au$_3$(MeN=COEt)$_3$}$_2$·{2,7-dinitro-9-fluorenone}, **3**, with 35% thermal contours for all non-hydrogen atoms. The hydrogen atom positions are not shown.

the 2 and 7 positions and larger angles (29.4, 38.4, 39.8, 42.3°) for the nitro groups in the 4 and 5 positions.

There is disorder in locations of the gold atoms in each of the two trimers. In addition to the positions of the trimeric gold complexes shown in Figure 3, alternate sites, which lie in the plane of the trimers and involve both rotation and translation, were found. Details are given in the Supporting Information. The orientations shown in the figures are those for the site with 85% occupancy. The atoms of the ligand atoms for these alternate orientations were not found, which is not surprising given the low electron density associated with these low occupancy sites.

(c) {Au$_3$(MeN=COEt)$_3$}$_2$·{2,7-dinitro-9-fluorenone}, 3. The asymmetric unit in the red crystals is comprised of two molecules of {Au$_3$(MeN=COEt)$_3$} and one of 2,7-dinitro-9-fluorenone. A drawing of these individual components is shown in Figure 4. The 2,7-dinitro-9-fluorenone molecule is nearly planar with the nitro groups lying in the plane of the carbon framework of the molecule. This is consistent with structural work on crystalline 2,7-dinitro-9-fluorenone itself.[36]

The two molecules of {Au$_3$(MeN=COEt)$_3$} associate with one another through close Au···Au contacts to form a slightly twisted, trigonal prismatic, Au$_6$ array as seen in Figure 4. One Au$_3$ triangle is twisted 7.7° with respect to the other Au$_3$ triangle. The two Au$_3$ triangles are nearly parallel; the angle between them is only 1.5°. Within the dimeric unit the two {Au$_3$(MeN=COEt)$_3$} units are arranged in a head-to-tail fashion so that carbon atoms and nitrogen atoms of the ligand bridges lie over each another. As seen in Table 1, the intermolecular Au···Au distances (3.2438(10), 3.2328(9), and 3.3545(9) Å) are shorter than the corresponding distance (3.3463(5) Å) in the infinite prismatic stack found in{Au$_3$(MeN=COMe)$_3$}.

The prismatic {Au$_3$(MeN=COEt)$_3$}$_2$ units are interleaved with 2,7-dinitro-9-fluorenone molecules to form columns in the solid state as seen in Figure 5.

(d) {Au$_3$(MeN=COEt)$_3$}$_2$·{2,4,7-trinitro-9-fluorenone}, 4. One molecule of {Au$_3$(MeN=COEt)$_3$} and half a molecule of 2,4,7-trinitro-9-fluorenone comprise the asymmetric unit in the red crystals of {Au$_3$(MeN=COEt)$_3$}$_2$·{2,4,7-trinitro-9-fluorenone}. Figure 6 shows views of these two components. The 2,4,7-trinitro-9-fluorenone molecule is situated on a crystallographic 2-fold axis and one of the two nitro groups (the one involving N(4)) is disordered and has only 50% site occupancy. The {Au$_3$(MeN=COEt)$_3$} molecule also suffers from disorder. The ethyl group attached to O(3) occupies two different positions as seen in Figure 6.

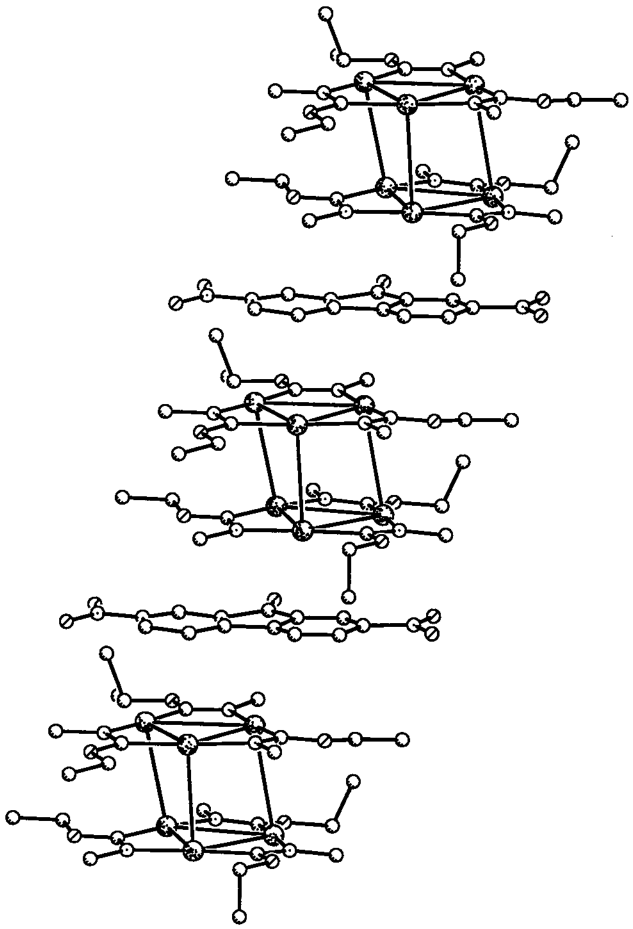

Figure 5. A view of the molecular packing that emphasizes the columnar structure of {Au$_3$(MeN=COEt)$_3$}$_2$·{2,7-dinitro-9-fluorenone}, **3**.

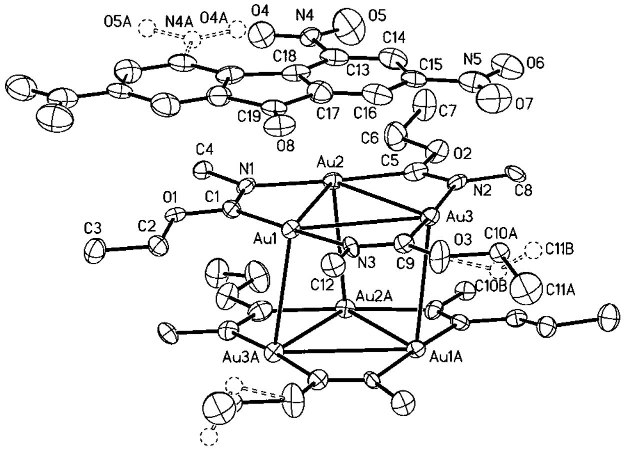

Figure 6. Drawings of the structures of the individual components in {Au$_3$(MeN=COEt)$_3$}$_2$·{2,4,7-trinitro-9-fluorenone}, **4**. Disordered portions in each component are shown with dashed lines. Anisotropic thermal ellipsoids are shown at the 50% probability level.

Figure 7 shows how the {Au$_3$(MeN=COEt)$_3$} and 2,4,7-trinitro-9-fluorenone molecules pack into columns in the solid state. Within these columns two gold trimers are assembled into a slightly twisted trigonal prism. The intermolecular Au···Au distances, 3.2200(11) and 3.2312(14) Å, are shorter than the intramolecular Au···Au distances, 3.2910(9) and 3.3175(11) Å. The planes of the two Au$_3$ triangles are nearly parallel with only a 0.9° angle between them.

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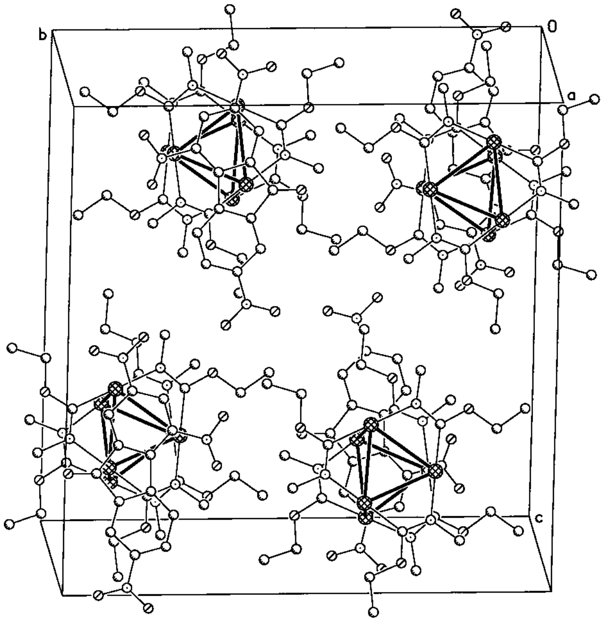


Figure 7. A drawing that shows the organization of the individual components into columns in crystalline $\{Au_3(MeN{=}COEt)_3\}_2\cdot\{$2,4,7-trinitro-9-fluorenone$\}$, **4**.

These prismatic Au_6 arrays are interleaved with 2,4,7-trinitro-9-fluorenone molecules in the stacks with the $\{Au_3(MeN{=}COEt)_3\}$ molecules lying over the nitro arene rings of the organic acceptor as seen in the other compounds reported here.

Spectroscopic Studies. The formations of red or deep yellow colored solutions and colored solids upon mixing solutions of the colorless $\{Au_3(MeN{=}COMe)_3\}$ or $\{Au_3(MeN{=}COEt)_3\}$ with the pale yellow electron acceptors, the nitro-fluorenones, are indicative of the presence of charge-transfer complexes. Relevant spectroscopic data for dichloromethane solutions of these compounds are shown in Figure 8. Part A compares the spectra of solutions of $\{Au_3(MeN{=}COMe)_3\}$ alone, 2,4,5,7-tetranitro-9-fluorenone alone, and a mixture of $\{Au_3(MeN{=}COMe)_3\}$ and 2,4,5,7-tetranitro-9-fluorenone, all at the same concentration. The spectrum of the mixture shows enhanced absorption at longer wavelengths, which is indicative of a charge-transfer interaction. Two shoulders at 580 and 470 nm are visible in the spectrum of the mixture. Part B of Figure 8 shows similar data for a dichloromethane solution of $\{Au_3(MeN{=}COEt)_3\}$ alone, 2,4,7-trinitro-9-fluorenone alone, and a mixture of $\{Au_3(MeN{=}COEt)_3\}$ and 2,4,7-trinitro-9-fluorenone, all at the same concentration. Two new absorptions at 600 and 490 nm appear in the spectrum of the mixture. These new features are readily assigned to the formation of charge-transfer complexes. Similar data for a mixture of $\{Au_3(MeN{=}COMe)_3\}$ and 2,4,7-trinitro-9-fluorenone show enhanced absorption in the 400−600 nm region with a shoulder at 460 nm. In contrast, the ^1H NMR spectrum of a mixture of $\{Au_3(MeN{=}COMe)_3\}$ and 2,4,5,7-tetranitro-9-fluorenone does not show any difference from the spectroscopic features of the individual components.

No luminescence has been observed from these solid charge-transfer adducts under conditions where $\{Au_3(MeN{=}COMe)_3\}$ is strongly luminescent. This is not surprising since the luminescence of $\{Au_3(MeN{=}COMe)_3\}$ is a property that is associated with the supramolecular organization in the solid. Thus, the prismatic columns seen in $\{Au_3(MeN{=}COMe)_3\}$ are not present in the new adducts reported here.

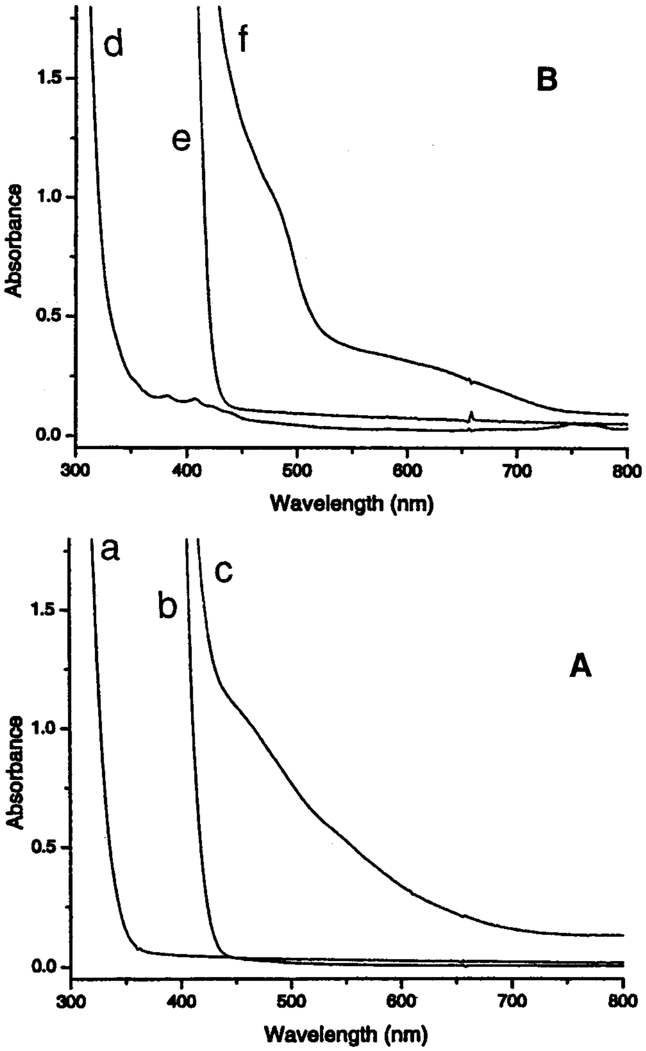


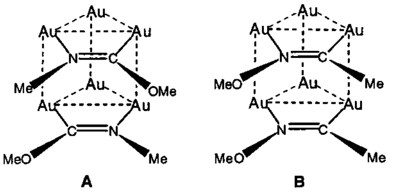
Figure 8. UV/vis absorption data for charge-transfer complexes: (A) a dichloromethane solution containing (a) 5.0 mM $\{Au_3(MeN{=}COMe)_3\}$ alone, (b) 5.0 mM 2,4,5,7-tetranitro-9-fluorenone alone, and (c) a mixture of 5.0 mM $\{Au_3(MeN{=}COMe)_3\}$ and 5.0 mM 2,4,5,7-tetranitro-9-fluorenone; (B) a dichloromethane solution containing (d) 5.0 mM $\{Au_3(MeN{=}COEt)_3\}$ alone, (e) 5.0 mM 2,4,7-trinitro-9-fluorenone alone, and (f) a mixture of 5.0 mM $\{Au_3(MeN{=}COEt)_3\}$ and 5.0 mM 2,4,7-trinitro-9-fluorenone.

Conclusions

The results presented here demonstrate that the gold trimers, $\{Au_3(MeN{=}COMe)_3\}$and $\{Au_3(MeN{=}COEt)_3\}$, can act as electron donors and do associate with organic electron acceptors. Stable crystalline adducts with three nitrofluorenones have been isolated and characterized crystallographically. The structures of these adducts with $\{Au_3(MeN{=}COMe)_3\}$ involve mixed stacks in which the gold trimers and the planar, or nearly planar, nitro-fluorenones are interleaved. In forming these solids, the columnar extended prismatic set of $Au\cdots Au$ interactions found in $\{Au_3(MeN{=}COMe)_3\}$ itself are no longer present. Thus, the formation of charge-transfer adducts can disrupt the aurophilic interactions present in crystalline $\{Au_3(MeN{=}COMe)_3\}$.

Most significantly, the structures of $\{Au_3(MeN{=}COEt)_3\}_2\cdot\{$2,7-dinitro-9-fluorenone$\}$ and $\{Au_3(MeN{=}COEt)_3\}_2\cdot\{$2,4,7-trinitro-9-fluorenone$\}$ reveal that aurophilic interactions can also be present in the charge-transfer adducts. Prismatic $\{Au_3(MeN{=}COEt)_3\}_2$ arrays with Au_6 cores are present in both $\{Au_3(MeN{=}COEt)_3\}_2\cdot\{$2,7-dinitro-9-fluorenone$\}$ and $\{Au_3(MeN{=}COEt)_3\}_2\cdot\{$2,7-dinitro-9-fluorenone$\}$. Thus, charge-transfer interactions

Chart 3



can be used to modify the structures of gold complexes where aurophilic interactions play a prominent role in structural organization. Within both of the prismatic $\{Au_3(MeN{=}COEt)_3\}_2$ arrays seen in Figures 4 and 6, the individual trimeric units adopt a head-to-tail arrangement as shown in structure **A** of Chart 3 rather than a head-to head arrangement as seen in structure **B** of Chart 3. For clarity in this chart, only the two ligands on the front of each Au_6 array are shown. The arrangement **A** may be favored because of alignment of the local dipoles in each C−Au−N unit, and each N=C unit places fragments of opposite polarity adjacent to one another. Notice that in the extended structure of $\{Au_3(MeN{=}COMe)_3\}$, the "flip" disorder[2] that is present in the location of the methyl and methoxy groups ensures that both the head-to-tail and head-to-head arrangements are mixed within the prismatic columns.

In this work the prismatic arrays with an Au_6 core have been obtained with $\{Au_3(MeN{=}COEt)_3\}$ but not with $\{Au_3(MeN{=}COMe)_3\}$. A number of factors are likely to be involved in this difference in behavior. We expect that the electronic difference between the two is small and may not be responsible for the difference. However, there is considerable difference in solubility between $\{Au_3(MeN{=}COEt)_3\}$ and $\{Au_3(MeN{=}COMe)_3\}$ with the former having much higher solubility in most solvents. On simple stoichiometric concerns, higher concentrations of the gold trimer are likely to be needed to prepare compounds with a 2:1 ratio of gold trimer to nitrofluorenone than those with a 1:1 ratio of gold trimer to nitrofluorenone. Consequently the higher solubility of $\{Au_3(MeN{=}COEt)_3\}$ may play a significant role in determining the nature of the adduct that crystallizes from solution. Additionally there is the issue of the solubility of the crystalline adduct itself. Low solubility of the adduct will favor its crystallization.

The nitrofluorenones have been extensively used as electron acceptors,[28−32] and a few other examples of donor/acceptor adducts with a nitrofluorenone have been characterized crystallographically. Only one compound, {nickel(II) etioporphyrin I}·2{2,4,5,7-tetranitro-9-fluorenone}, involves a transition metal containing component.[37] In this solid the {nickel(II) etioporphyrin I} component is sandwiched in a face-to-face fashion between two molecules of {2,4,5,7-tetranitro-9-fluorenone}. There are no other face-to-face contacts beyond those within this triplet of molecules in this solid. Other donor/acceptor complexes involve organic donors and have the donors and acceptors arranged in alternating fashion into columns. Such compounds include the following: {2,4,7-trinitrofluorenone}·{hexamethylbenzene},[38] 2,4,7-trinitrofluorenone·2,6-dimethylnaphthalene,[29] 2,4,7-trinitrofluorenone·2,7-dimethyl-naphthalene,[29] {2,2′-bis-1,3dithiole}·{2,7-dinotro-9-fluorenone},[39] {1-ethylnaphthalene}· {2,4,5,7-tetranitro-9-fluorenone},[40] {3,6-dimethylphenanthrene}·{2,4,5,7-tetranitro-9-fluorenone},[40] {2-ethylnaphthalene}·{2,4,5,7-tetranitro-9-fluorenone},[41] and {tetrakis(phenylethynyl)ethane·2{2,4,7-trinitro-9-fluorenone}.[42,43]

After the experimental work reported here was completed, we learned of another type of donor/acceptor compound formed by the gold(I) trimer, $\{Au_3(p\text{-tol}N{=}COEt)_3\}$ (and by a related complex of the type **1** shown in Chart 1).[44] In these compounds, which are luminescent, the inorganic acceptor, $\{Hg_3(C_6H_4)_3\}$, was shown to form structures in which two molecules of the gold(I) trimer surrounded each molecule of $\{Hg_3(C_6H_4)_3\}$. These units are then organized into columns with a repeating pattern of $\{Au_3Hg_3Au_3\}_n$. There are short Au···Hg (ca. 3.24 Å) and Au···Au (ca. 3.3−3.5 Å) contacts along the chains in both of the solids.

Experimental Section

Materials. Dichloromethane, methanol, ethanol, ethyl ether, and other organic solvents were dried over molecular sieves and then purified by standard methods. Hydrogen tetrachloroaurate(III) hydrate was purchased from Pressure Chemical Co. Triphenylphosphine, 2,7-dinitro-9-fluorenone, 2,4,7-trinitro-9-fluorenone, and 2,4,5,7-tetranitro-9-fluorenone were purchased from Aldrich and all were used as received. Literature procedures were used for preparation of $AuCl(PPh_3)$,[45] methyl isocyanide,[46,47] and $\{Au_3(MeN{=}COMe)_3\}$.[1]

$\{Au_3(MeN{=}COEt)_3\}$. This compound was prepared according to a modification of the published procedure for the preparation of $\{Au_3(MeN{=}COMe)_3\}$.[1] A solution of potassium hydroxide (0.18 g, 3.2 mmol) in 20 mL of ethanol was added to a rapidly stirred suspension of $AuCl(PPh_3)$ (1.38 g, 2.8 mmol) in 30 mL of ethanol. Subsequently, excess methyl isocyanide (0.40 mL, 6.0 mmol) was added. The suspension immediately dissolved to produce a transparent, colorless solution. The solution continued to be stirred for 20 h at room temperature, and a little white precipitate formed. After filtration, the filtrate was allowed to evaporate slowly for a few days. A colorless, hair-like, crystalline product formed on the walls of the flask during this period. Additional quantities of the product were obtained by washing the solid residue from the filtration with diethyl ether. The diethyl ether extract was allowed to evaporate slowly to form an additional crop of colorless, hair-like crystals on the wall of the flask. Both of the materials were collected and dried in a vacuum. The yield of $\{Au_3(MeN{=}COEt)_3\}$ was 35 mg (41%). Unlike $\{Au_3(MeN{=}COMe)_3\}$, which is stable and not soluble in ethyl ether and alcohol solvents, $\{Au_3(MeN{=}COEt)_3\}$ is light sensitive and soluble in most organic solvents including not only dichloromethane and chloroform but also diethyl ether and ethanol ^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 4.45 (6H q), 2.99 (9H, s), 1.35 (9H, t) ppm. IR (KBr pellet, cm^{-1}): 2973 (w), 2922 (m), 2867 (w), 1652 (m), 1565 (vs), 1559 (vs), 1447 (w), 1426 (w), 1383 (w), 1194 (s), 1140 (s), 1110 (vs), 1055 (m), 1008 (w), 747 (w), 692 (w), 523(w).

$\{Au_3(MeN{=}COMe)_3\}$·{2,4,7-trinitro-9-fluorenone}, 1. A pale yellow solution of 2,4,7-trinitro-9-fluorenone (32 mg, 0.1 mmol) in 10 mL of dichloromethane was added to a colorless solution of $\{Au_3(MeN{=}COMe)_3\}$ (81 mg, 0.10 mmol) in 25 mL of dichloromethane. The solution immediately became orange-red in color. After the solution was shaken for a few minutes, it was filtered, and the filtrate was

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Table 2. Crystallographic Data for Compounds **1**−**4**

	$\{Au_3(MeN{=}COMe)_3\}\cdot$ {2,4,7-trinitro-9-fluorenone} (**1**)	$\{Au_3(MeN{=}COMe)_3\}\cdot$ {2,4,5,7-tetranitro-9-fluorenone} (**2**)	$\{Au_3(MeN{=}COEt)_3\}_2\cdot$ {2,7-dinitro-9-fluorenone} (**3**)	$\{Au_3(MeN{=}COEt)_3\}_2\cdot$ {2,4,7-trinitro-9-fluorenone} (**4**)
formula	$C_{22}H_{23}Au_3N_6O_{10}$	$C_{22}H_{22}Au_3N_7O_{12}$	$C_{37}H_{54}Au_6N_8O_{11}$	$C_{37}H_{53}Au_6N_9O_{13}$
fw	1122.36	1167.37	1968.68	2013.68
a, Å	21.2899(8)	11.4386(8)	10.7378(8)	10.6362(9)
b, Å	6.7133(3)	33.904(2)	10.8948(9)	20.580(2)
c, Å	19.9781(7)	15.5030(10)	22.4780(17)	22.095(2)
α, deg	90	90	88.799(2)	90
β, deg	108.2330(10)	106.4820(10)	84.820(2)	93.72(2)
γ, deg	90	90	63.7300(10)	90
V, Å^3	2749	5765.3(7)	2347.9(3)	4826.2(8)
Z	4	8	2	4
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$
T, °C	90(2)	90(2)	90(2)	90(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
ρ, g/cm^3	2.749	2.690	2.785	2.771
μ, cm^{-1}	16.255	15.305	18.738	18.238
R_1 (obsd data)	0.033	0.080	0.067	0.057
$wR2$ (all data, F^2 refinement)	0.0744	0.168	0.188	0.1312

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

condensed under the reduced pressure. The concentrated solution was carefully layered over ethanol and allowed to stand for several days at room temperature. Yellow crystals of the product gradually precipitated. The crystals were collected, washed with ethyl ether, and dried in a vacuum to produce 97 mg (86%) of $\{Au_3(CH_3N{=}COCH_3)_3\}\cdot$\{2,4,7-trinitro-9-fluorenone\}, **1**. ^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 9.03 (1H, s), 8.82 (1H, s), 8.67 (1H, s), 8.56 (1H, d), 8.37 (1H, d), 3.98 (9H, s), 2.92 (9H, s) ppm. IR (KBr pellet, cm^{-1}): 3095 (w), 2917 (m), 2850 (w), 1734 (s), 1545 (vs), 1528 (m), 1340 (vs), 1226 (m), 1135 (m), 1083 (w),1042 (w), 838 (w), 730 (w).

$\{Au_3(MeN{=}COMe)_3\}\cdot$\{2,4,5,7-tetranitro-9-fluorenone\}, 2. A pale yellow solution of 2,4,5,7-tetranitro-9-fluorenone (36 mg, 0.1 mmol) in 15 mL of dichloromethane was added to a colorless solution of $\{Au_3(MeN{=}COMe)_3\}$ (81 mg, 0.10 mmol) in 25 mL of dichloromethane at room temperature. After the solution was shaken for a few minutes, the reaction mixture became brown in color. After filtration, the brown filtrate was condensed under reduced pressure. Ethyl ether was diffused into the brown solution over a period of one week. The red needles of the crystalline product were collected, washed with ethyl ether, and dried in a vacuum to produce 106 mg (91%) of $\{Au_3(MeN{=}COMe)_3\}\cdot$\{2,4,5,7-tetranitro-9-fluorenone\}, **2**. ^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 9.03 (2H, s), 8.89 (2H, s) 3.97 (9H s), 2.92 (9H, s) ppm. IR (KBr pellet cm^{-1}): 3092 (w), 2919 (m), 2855 (m), 1738 (w), 1616 (m), 1549 (s), 1536 (vs), 1456 (w), 1344 (s), 1226 (m), 1138 (m), 831 (w), 728 (w).

$\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,7-dinitro-9-fluorenone\}, 3. A yellow solution of 2,7-dinitro-9-fluorenone (14 mg, 0.05 mmol) in 10 mL of dichloromethane was added to a colorless solution of $\{Au_3(MeN{=}COEt)_3\}$ (85 mg, 0.10 mmol) in 30 mL of dichloromethane. The color of the solution was not changed too much in the initial mixing. After the solution was shaken for a few minutes, the solution was filtered and then allowed to slowly evaporate at room temperature for a few days. The red crystals which deposited during this period were collected, washed with hexane, and dried in a vacuum to afford 77 mg (78%) of $\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,7-dinitro-9-fluorenone\}, **3**. ^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 8.59 (2H, s), 8.53 (2H, d), 7.88 (2H, d), 4.46 (12H, q), 2.93 (18H, s), 1.35 (18H, t). IR (KBr pellet, cm^{-1}): 2977 (m), 2920 (m), 2875 (w), 1724 (s), 1605 (w), 1556 (vs), 1521 (s), 1439 (w), 1339 (vs), 1199 (s), 1156 (s), 1121 (m), 1102 (m), 1051 (w), 839 (w), 734 (m).

$\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,4,7-trinitro-9-fluorenone\}, 4. An orange solution of 16 mg (0.05 mmol) of 2,4,7-trinitro-9-fluorenone in 10 mL of dichloromethane was added to a colorless solution of $\{Au_3(MeN{=}COEt)_3\}_2$ (85 g, 0.10 mmol) in 30 mL of dichloromethane. The resulting orange-red solution was filtered and condensed under the reduced pressure. The solution was carefully layered over ethanol and allowed to stand for several days at room temperature. The red crystals which deposited during this period were collected, washed with hexane, and dried in a vacuum to produce 79 g (78%) of $\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,4,7-trinitro-9-fluorenone\}, **4**. ^1H NMR (300.1 MHz, 298 K, $CDCl_3$): δ 9.03 (1H, s), 8.82 (1H, s), 8.67 (1H, s), 8.56 (1H, d), 8.37 (1H, d), 4.45 (12H q), 2.93 (18H, s), 1.35 (18H, t) ppm. IR (KBr pellet, cm^{-1}): 2972 (w), 2925 (m), 2874 (w), 1733 (s), 1558 (vs), 1554 (vs), 1522 (m), 1436 (w), 1340 (vs), 1199 (m), 1157 (m), 1103 (w), 837 (w), 667 (w).

Physical Measurement. ^1H NMR spectra were recorded for chloroform-*d* solutions on a General Electric QE-300 NMR spectrometer operating at 300 MHz with an external tetramethylsilane standard and the high-field positive convention for chemical shifts. Infrared spectra were recorded as pressed KBr pellets or mineral oil mulls on a Matteson Galaxie Series FTIR 3000 spectrometer. Electronic absorption spectra were recorded with a Hewlett-Packard 8450A diode array spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrophotometer.

X-ray Crystallography and Data Collection. The crystals were removed from the glass tubes in which they we grown together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on the microscope slide. Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo Kα radiation at 90(2) K. Check reflections were stable throughout data collection. Crystal data are given in Table 2.

The structures were solved by Patterson methods and refined by using all data (based on F^2) with the SHELXTL 5.1 software. A semiempirical method utilizing equivalents was employed to correct for absorption.[48] Hydrogen atoms were added geometrically and refined with a riding model.

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Supporting Information Available: X-ray crystallographic files for $\{Au_3(MeN{=}COMe)_3\}\cdot$\{2, 4, 7-trinitro-9-fluorenone\}, $\{Au_3(MeN{=}COMe)_3\}\cdot$\{2,4,5,7-tetranitro-9-fluorenone\}, $\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,7-dinitro-9-fluorenone\}, and $\{Au_3(MeN{=}COEt)_3\}_2\cdot$\{2,4,7-trinitro-9-fluorenone\} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(48) Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *A51*, 33.