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Intermolecular Interactions in Polymorphs of Trinuclear Gold(I) Complexes: Insight into the Solvoluminescence of $\mathrm{Au^I_3(MeN{=}COMe)_3}$

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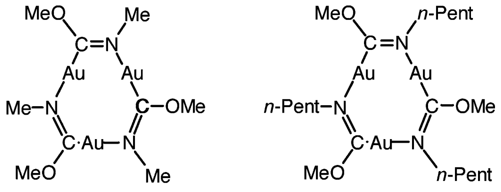
The trinuclear complex, $\mathrm{Au^I_3(MeN{=}COMe)_3}$, which displays a number of remarkable properties including solvoluminescence, has been found to crystallize as three polymorphs. The new triclinic and monoclinic polymorphs crystallized as colorless blocks, whereas the original hexagonal polymorph formed colorless needles. These polymorphs differ in the manner in which the nearly planar molecules pack and in the nature of the aurophilic interactions between them. Each of the three polymorphs of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ shows a distinctive emission spectrum, but only the original hexagonal polymorph shows the low-energy emission that is responsible for its solvoluminescence. Colorless $\mathrm{Au^I_3}$(*n*-PentN=COMe)$_3$ crystallized from diethyl ether as needles of an orthorhombic polymorph and blocks of a triclinic polymorph. These polymorphs differ in the orientation of the *n*-Pent substituents, in the orientation of the trimers with respect to one another, and in the nature of the aurophilic interactions between the molecules. Only the triclinic polymorph of $\mathrm{Au^I_3}$(*n*-PentN=COMe)$_3$ shows luminescence at room temperature, but it is not solvoluminescent. Colorless $\mathrm{Au^I_3}$(*i*-PrN=COMe)$_3$ has also been prepared and crystallographically characterized. The isopropyl groups protrude out of the plane of the nine-membered ring and prevent self-association. The closest Au···Au contact between molecules is 6.417 Å. Crystalline $\mathrm{Au^I_3}$(*i*-PrN=COMe)$_3$ is not luminescent at room temperature.

Introduction

The colorless gold trimer, $\mathrm{Au^I_3(MeN{=}COMe)_3}$,[1] whose molecular structure is shown in Chart 1, displays a number of interesting properties. Upon irradiation of a crystalline sample of the complex with near UV light, a yellow emission with multiexponential decay and a lifetime as long as 31 s is easily seen visually.[2,3] When a solvent such as chloroform or dichloromethane is dropped onto previously irradiated crystals of $\mathrm{Au^I_3(MeN{=}COMe)_3}$, a bright burst of light that is readily detected by the human eye is produced. Because the intensity of this emission is greatest for those liquids that are good solvents for $\mathrm{Au^I_3(MeN{=}COMe)_3}$, the phenomenon has been termed solvoluminescence. Oxidation of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ with diiodine or dibromine produces the $\mathrm{Au_3X_{\mathit{n}}(MeN{=}COMe)_3}$ (n = 2, 4, or 6) series of complexes in which the two-coordinate gold(I) ions are successively oxidized to four-coordinate gold(III) centers.[1,4] Upon exposure to solutions of organic acceptors such as nitrofluorenones, $\mathrm{Au^I_3(MeN{=}COMe)_3}$ forms crystalline charge-transfer adducts in which the planar donors and acceptors are interleaved.[5]

Chart 1



{$\mathrm{Au_3(MeN{=}COMe)_3}$} {$\mathrm{Au_3}$(*n*-PentN=COMe)$_3$}

It has been suggested previously that the remarkable luminescence and solvoluminescence of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ comes from the unique organization of the planar molecules in the solid state.[2,3] Chart 2 shows common structural motifs

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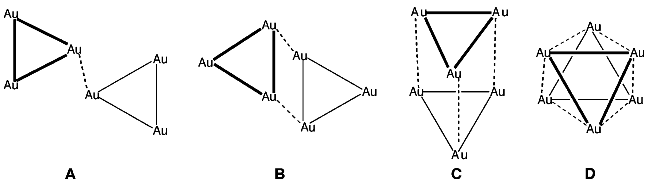
Chart 2



by which a pair of trinuclear complexes of the type discussed in this paper can undergo self-association. In this chart, the trinuclear complexes are represented by triangles with the gold atoms at the apexes. The aurophilic interactions between molecules are shown as dashed lines, and the bridging ligands are not shown. These arrangements include the situation shown in **A**, where a single aurophilic interaction connects the pair of molecules, the arrangement shown in **B**, where there are two aurophilic interactions between the trimers, and the prismatic arrangement **C**, where there are three aurophilic interactions between the pair of trimers. Additionally, the prismatic arrangement can be twisted to form the offset (octahedral) array shown as **D**. Finally, it is also possible that no aurophilic interactions exist between the trinuclear complexes.

Earlier work demonstrated that colorless $Au^I_3(MeN{=}COMe)_3$ crystallizes as needles in the hexagonal space group *P*6/*m*. The individual planar molecules aggregate along the *c* axis to form extended trigonal prismatic stacks of type **C**. In these stacks, the three gold atoms of one molecule lie directly above and below neighboring molecules to form an infinite column. The intermolecular Au···Au distance in these prismatic stacks is 3.346(1) Å, and thus attractive aurophilic interactions[6,7] between the gold centers are present within the columns. Within each molecule, there are additional Au···Au contacts with a distance of 3.308(2) Å. Nevertheless, within the molecule, the C−Au−N angles are all 180°, and there is no evidence that these Au···Au interactions distort the molecular structure. In addition to these ordered prismatic stacks, there are other disordered stacks in which there are two sets of positions (one offset by 60° from the other) for the gold triangles that have structural motif **D**. Within the crystal, there are two prismatic stacks for every offset stack. Both stacks run parallel to the crystallographic *c* axis.

The aurophilic interactions seen in the solid-state structures of many two-coordinate Au(I) complexes are weakly attractive with bond energies of ca. 7−11 kcal/mol, i.e., similar to the energies of hydrogen bonds.[8,9] For two-coordinate gold(I) complexes, these weak aurophilic interactions compete with other forces in the solid state to produce the observed structures. The formation of polymorphs,[10,11] crystals in which identical molecules (or ions) pack in various fashions in unit cells of differing dimensions, is highly likely for closed shell Au(I) complexes where a number of different and competing factors determine the nature of the Au···Au interactions that are frequently, but not always, present.

For example, this laboratory has recently shown that the $[(C_6H_{11}NC)_2Au^I](PF_6)$ salt exists in two polymorphic forms with differing, but close, contacts between the cations, which form extended chains through Au···Au contacts.[12] In the colorless polymorph, the gold cations form linear chains with a short Au···Au contact (3.1822(3) Å). The structure of the yellow polymorph is more complicated. It consists of four independent cations that are linked in kinked slightly helical chains. Within this arrangement, the Au···Au contacts are unusually short (2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å) particularly considering that the interactions involve cations, not neutral molecules. Both polymorphs are luminescent at 298 K. The colorless form has an emission at a λ_{max} of 424 nm, while the yellow polymorph produces an emission at 480 nm.

Additionally, two polymorphs of $(Me_2PhP)Au^ICl$ have been identified.[13,14] In one polymorph, the molecules crystallize as dimers with an Au···Au separation of 3.230(2) Å, while in the other polymorph, a trimer is present with Au···Au separations of 3.091(2) and 3.120(2) Å.

Here, we report that $Au^I_3(MeN{=}COMe)_3$ and $Au^I_3(n\text{-}PentN{=}COMe)_3$ form polymorphs in which the nature of the Au···Au contacts among the molecules differ. The luminescence of the polymorphs also varies.

Results

Crystallographic Characterization of Three Polymorphs of $Au^I_3(MeN{=}COMe)_3$. During the growth of crystals of $Au^I_3(MeN{=}COMe)_3$, we have noted that samples of the complex which were pure on the basis of their ^1H NMR spectra formed crystals with varying luminescence. Most samples produced the yellow luminescence that was described in our earlier studies,[2,3] while others showed a blue white luminescence;a few crystals with a pink luminescence have also been seen. Figure 1 shows a photograph of the luminescence from a particular sample of $Au^I_3(MeN{=}COMe)_3$ taken while being irradiated with a UV lamp. That sample was obtained by evaporation of a dichloromethane solution of the complex. This process produced a region of crystals with the expected yellow luminescence and a group of crystals at the bottom of the flask that showed a blue-white luminescence. Unfortunately, the crystals in this sample were too small to use to obtain single-crystal X-ray diffraction data.

However, we have managed to obtain two samples of the new polymorphs that were suitable for X-ray data collection. Both were obtained by evaporation from a dichloromethane solution, and both are polymorphs of $Au^I_3(MeN{=}COMe)_3$, as shown by the crystal data in Table 1. The new triclinic

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Table 1. Crystallographic Data for Gold(I) Compounds

	$\mathrm{Au_3(MeN{=}COMe)_3}$	$\mathrm{Au_3(MeN{=}COMe)_3}$	$\mathrm{Au_3(MeN{=}COMe)_3}$
	hexagonal[a]	triclinic	monoclinic
color/habit	colorless needle	colorless block	colorless block
formula	$\mathrm{C_9H_{18}Au_3N_3O_3}$	$\mathrm{C_9H_{18}Au_3N_3O_3}$	$\mathrm{C_9H_{18}Au_3N_3O_3}$
fw	807.16	807.16	807.16
cryst syst	hexagonal	triclinic	monoclinic
space group	$P6/m$	$P\bar{1}$	$C2/c$
a (Å)	19.410(4)	8.012(3)	33.573(11)
b (Å)	19.410(4)	9.903(4)	19.384(8)
c (Å)	3.3463(5)	10.584(4)	21.631(8)
α (deg)	90	64.758(12)	90
β (deg)	90	71.436(13)	111.832(13)
γ (deg)	120	74.256(12)	90
V (Å^3)	1091.8(4)	711.0(5)	13067
Z	3	2	36
T (°C)	130(2)	90(2)	90(2)
λ (Å)	1.54178	0.71073	0.71073
ρ (g/cm^3)	3.683	3.770	3.693
μ (cm^{-1})	55.8	30.877	30.24
R_1 (observed data)[b]	0.064	0.033	0.145
wR2 (all data, F^2 refinement)[c]	0.165	0.082	0.400

	$\mathrm{Au_3(\textit{n}\text{-}PeN{=}COMe)_3}$	$\mathrm{Au_3(\textit{n}\text{-}PeN{=}COMe)_3}$	$\mathrm{Au_3(\textit{i}\text{-}PrN{=}COMe)_3}$
cryst syst	orthorhombic (needle)	triclinic (block)	orthorhombic
color/habit	colorless needle	colorless block	colorless block
formula	$\mathrm{C_{21}H_{42}Au_3N_3O_3}$	$\mathrm{C_{21}H_{42}Au_3N_3O_3}$	$\mathrm{C_{15}H_{30}Au_3N_3O_3}$
fw	975.48	975.48	891.32
space group	$Pbcn$	$P\bar{1}$	$Pca2_1$
a (Å)	23.066(12)	14.9537(12)	13.0563(7)
b (Å)	24.294(13)	18.6091(15)	13.9550(7)
c (Å)	9.663(5)	21.0647(17)	11.5493(6)
α (deg)	90	109.237(6)	90
β (deg)	90	90.151(4)	90
γ (deg)	90	104.539(5)	90
V (Å^3)	5415(5)	5333.8(7)	2104.29(19)
Z	8	8	4
T (°C)	90(2)	90(2)	91(2)
λ (Å)	0.71073	0.71073	0.71073
ρ (g/cm^3)	2.393	2.429	2.813
μ (cm^{-1})	16.24	16.487	20.881
R_1 (observed data)[b]	0.096	0.062	0.022
wR2 (all data, F^2 refinement)[c]	0.278	0.178	0.056

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

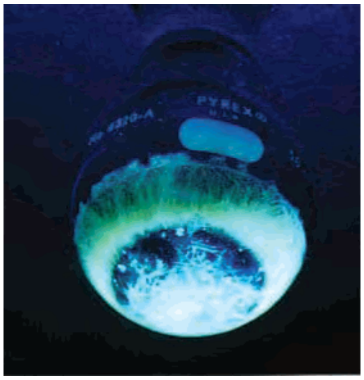

Figure 1. Photograph of the luminescence from a flask containing a mixture of the polymorphs of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ taken while the sample was irradiated with a hand-held UV lamp.

and monoclinic polymorphs crystallized as colorless blocks, whereas as the original hexagonal polymorph formed colorless needles. The triclinic polymorph can also be obtained by diffusion of diethyl ether into a dichloromethane solution of the complex. Dissolution of a sample of the triclinic polymorph in dichloromethane followed by evaporation leads to the formation of a mixture of the hexagonal and triclinic polymorphs. Unfortunately, we have not been able to discern those features in the crystallization process that lead to the formation of the monoclinic polymorph. This is not an unusual situation with polymorphs, which have been known to vanish.[15] In our hands, the hexagonal polymorph reported earlier is most frequently found when dichloromethane solutions of the complex evaporate.

The asymmetric unit of the triclinic polymorph of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ contains one trimeric molecule whose molecular structure is entirely analogous to that reported earlier for the molecules in the ordered stacks in the hexagonal polymorph of this substance. Part A of Figure 2 shows a drawing of the nearly planar molecule. However, while the hexagonal polymorph showed orientational disorder in the location of the peripheral methyl and methoxy groups, the trinuclear molecule in the triclinic polymorph is entirely ordered. Selected interatomic distances and angles for both the hexagonal and trigonal polymorphs of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ are presented in Table 2.

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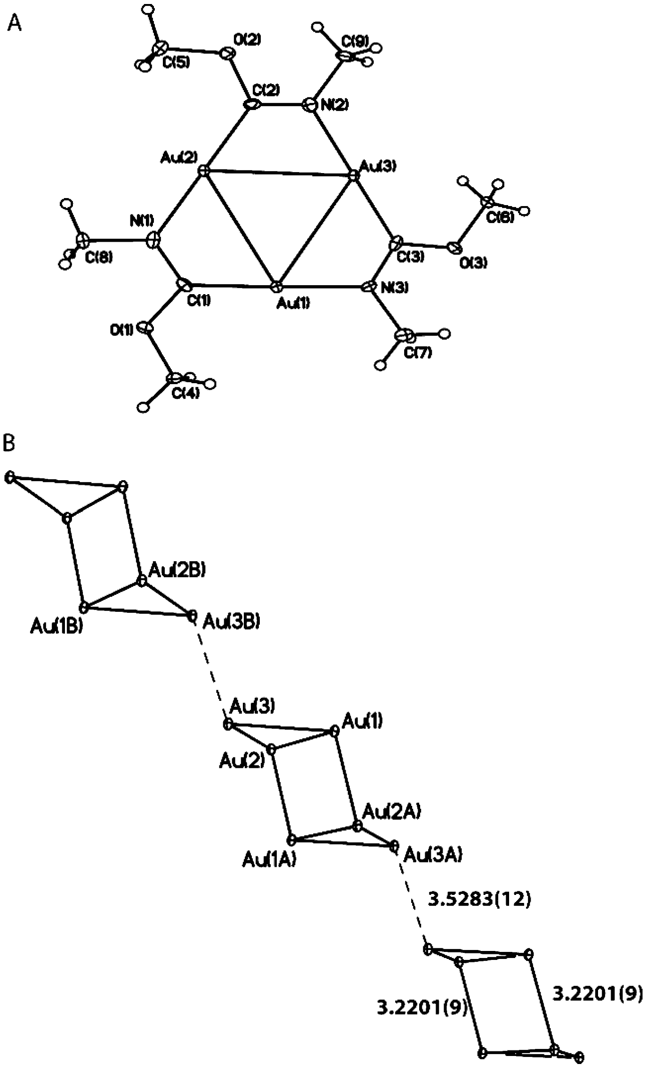

Figure 2. (A) Drawing of $Au^I_3(MeN{=}COMe)_3$ in the triclinic polymorph with 30% thermal ellipsoids. Intramolecular Au···Au distances are Au1···Au2, 3.3395(13); Au2···Au3, 3.3162(12); and Au1···Au3, 3.3394(11) Å. (B) Drawing showing the interactions between molecules in the triclinic polymorph of $Au^I_3(MeN{=}COMe)_3$.

Part B of Figure 2 shows the interactions between molecules in the triclinic polymorph. A pair of the cyclic trimers associate about a center of symmetry which results in two equivalent Au···Au interactions that involve Au1 in one molecule and Au2 in the adjacent molecule. This Au1···Au2A distance is 3.2201(9) Å. Furthermore, these pairs of molecules interact with neighboring pairs through additional Au···Au contacts that involve the other gold atom, Au3. The Au3···Au3A distance (3.583(12) Å) is significantly longer than the Au1···Au2A distance. Thus, each gold atom in the triclinic polymorph is involved in only one out-of-plane Au···Au interaction. In contrast, in the ordered prismatic stacks in the hexagonal polymorph of $Au^I_3(MeN{=}COMe)_3$, each gold atom is involved in two out-of-plane Au···Au interactions with neighboring molecules.

Only poorly diffracting crystals of the monoclinic polymorph of $Au^I_3(MeN{=}COMe)_3$ were found. These appear to contain a stacking fault and may have been twinned. Nevertheless, it was possible to locate the gold atoms and from those positions infer the molecular positions. The monoclinic polymorph contains 13.5 gold atoms in the asymmetric unit. The arrangement of these gold atoms within the unit cell is shown in Figure 3. Nine of the 13.5 gold atoms compose a prismatic stack that contains three of the trinuclear molecules. The average out-of-plane Au···Au distance in this stack is 3.28(3) Å. Each of these stacks is corner-linked to another stack to form an infinite chain that runs parallel to the *c* axis. However, the Au7···Au3A distance involved in this corner-linked arrangement is rather long, 3.65(3) Å. The remaining 4.5 gold atoms form half of a second similar prismatic stack which is grown by the application of a crystallographic 2-fold operation. The average out-of-plane Au···Au distance in this second stack (3.28(3) Å) is identical to that in the first stack. Each of these stacks is also corner-linked to another stack to form an infinite chain that runs parallel to the *c* axis. The Au11···Au11′ distance involved in this corner-linking is 3.48(3) Å.

Luminescence from the Polymorphs of $Au^I_3(MeN{=}COMe)_3$. Each of the three polymorphs of $Au^I_3(MeN{=}COMe)_3$ is luminescent, but each one also shows a distinctive emission spectrum. Relevant data obtained at room temperature are shown in Figure 4.

Under conventional fluorimetry, crystals of the hexagonal polymorph show dual luminescence at 450 nm and a low-energy shoulder at 520 nm, as seen in Part A of Figure 4. Previous work showed that the low-energy emission has a long-lived multiexponential decay, while the high-energy emission decays with a lifetime of ca. 1 ms.[2]

Crystals of the triclinic polymorph show a bluish luminescence. The emission and excitation spectra from a polycrystalline sample are shown in part B of Figure 4. The emission spectrum consists of a single emission at 444 nm. Most significantly, there is no counterpart for the low-energy long-lived emission found for the hexagonal polymorph. The triclinic polymorph is not solvoluminescent.

Crystals of the monoclinic polymorph are also luminescent. The emission and excitation spectra from a block are shown in part C of Figure 4. The emission spectrum consists of a single emission at 431 nm. Again, there is no counterpart for the low-energy long-lived emission found for the hexagonal polymorph. The excitation maximum occurs at 390 nm, which is red-shifted considerably from the excitation maximum for polymorph B which appears at 349 nm. The monoclinic polymorph is not solvoluminescent.

Crystallographic Characteristics of Two Polymorphs of Au^I_3(*n*-PentN$=$COMe)$_3$. Colorless Au^I_3(*n*-PentN$=$COMe)$_3$ was obtained by the reaction of a methanol solution of potassium hydroxide with $(Ph_3As)Au^ICl$ and *n*-pentyl isocyanide. Crystals were grown by evaporation of a diethyl ether solution of the complex. Two different crystal morphologies appeared in the same sample. These were found to be different polymorphs.

Crystals of the orthorhombic polymorph (needles) contain one independent trinuclear gold(I) complex in the asymmetric unit. Parts A and B of Figure 5 show front and side views of the molecule. Two of the *n*-pentyl groups lie parallel to the plane of the nine-membered ring, while the third *n*-pentyl

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Trinuclear Gold(I) Complexes

	$\mathrm{Au^I_3(MeN{=}COMe)_3}$[a] needle hexagonal	$\mathrm{Au^I_3(MeN{=}COMe)_3}$ block triclinic	$\mathrm{Au^I_3(}$*n*$\mathrm{\text{-}PentN{=}COMe)_3}$ needle ortho-rhombic	$\mathrm{Au^I_3(}$*n*$\mathrm{\text{-}PentN{=}COMe)_3}$ block triclinic			
				molecule #1	molecule #2	molecule #3	molecule #4
Au−C	2.00(1)	1.974(8)	2.05(4)	1.982(9)	1.974(9)	2.004(10)	1.979(11)
		1.980(8)	2.00(4)	1.976(11)	2.006(10)	1.994(11)	1.979(12)
		1.994(8)	1.98(4)	1.999(10)	2.024(10)	1.991(10)	1.993(11)
Au−N	2.03(1)	2.051(7)	2.10(3)	2.068(8)	2.033(8)	2.052(8)	2.063(8)
		2.048(7)	2.12(3)	2.062(9)	2.052(8)	2.052(8)	2.055(9)
		2.056(7)	2.09(3)	2.051(8)	2.058(9)	2.057(8)	2.062(9)
C═N	1.29(2)	1.312(11)	1.24(5)	1.330(12)	1.287(13)	1.326(13)	1.298(13)
		1.288(11)	1.25(5)	1.309(13)	1.357(14)	1.313(12)	1.314(13)
		1.279(11)	1.35(5)	1.313(13)	1.285(13)	1.285(13)	1.310(14)
Au⋯Au (intra)	3.308(2)	3.3395(13)	3.315(3)	3.2810(6)	3.2919(6)	3.3008(6)	3.2908(6)
		3.2201(9)	3.260(2)	3.2862(6)	3.3087(6)	3.3265(6)	3.2986(6)
		3.3162(12)	3.332(2)	3.3289(6)	3.3066(6)	3.3146(6)	3.3448(6)
C−Au−N	180	175.7(3)	177.8(14)	176.5(4)	177.1(4)	178.8(4)	178.5(4)
		176.1(3)	178.8(17)	175.3(4)	177.3(4)	179.6(4)	179.7(4)
		177.2(3)	178.8(14)	179.2(4)	175.6(3)	177.4(4)	179.7(4)

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

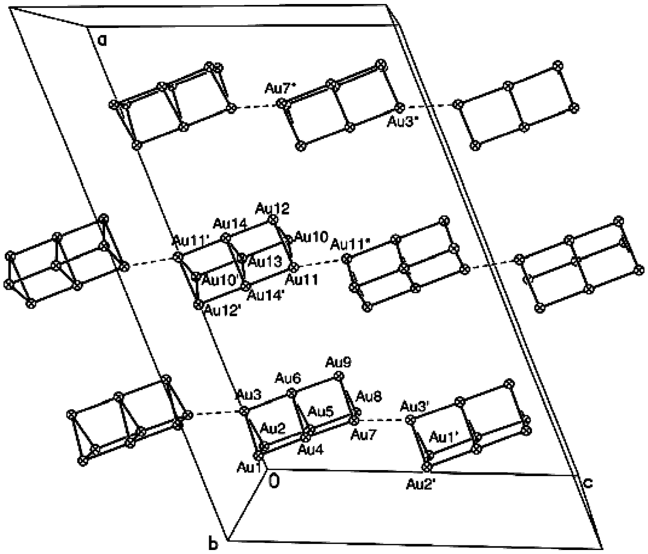

Figure 3. Drawing of the molecular orientations in the monoclinic polymorph of $\mathrm{Au^I_3(MeN{=}COMe)_3}$. Only the positions of the gold atoms are shown.

group protrudes almost perpendicularly from the plane. That group shows a high degree of thermal motion. The intramolecular Au⋯Au distances are 3.315(3), 3.260(2), and 3.332(2) Å. Other interatomic distances and angles are given in Table 2. The core geometry of this trimer is similar to that of $\mathrm{Au^I_3(MeN{=}COMe)_3}$, as expected.

Figure 6 shows how the molecules in the orthorhombic polymorph interact to form a stair-step arrangement. In this figure only the positions of the gold atoms are shown. Each molecule forms contacts with neighboring molecules through Au⋯Au interactions with a rather long Au⋯Au distance of 3.618(2) Å. The molecules pack so that the protruding *n*-pentyl groups of adjacent molecules are opposite each other. This stair-step mode of aggregation has been seen in the compound $\mathrm{Au^I_3(MeOC{=}NCH_2Ph)_3}$, which packs in a similar fashion, although with varying and generally much longer distances between the gold centers in neighboring molecules.[16] These distances range from to 3.662 to 4.100 Å for contacts between the eight crystallographically independent molecules present.

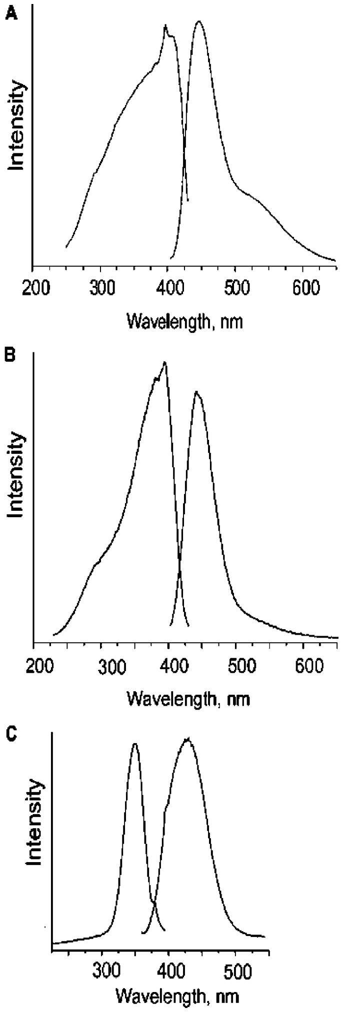

Figure 4. Comparisons of the emission and excitation spectra of the polymorphs of $\mathrm{Au^I_3(MeN{=}COMe)_3}$ at 298 K: (A) hexagonal polymorph, (B) triclinic polymorph, and (C) monoclinic polymorph.

The triclinic polymorph of $\mathrm{Au^I_3(}$*n*$\mathrm{\text{-}PentN{=}COMe)_3}$ contains four independent molecules in the asymmetric unit. All four have their *n*-pentyl groups lying near the plane of the three gold atoms and have similar structures. Part C of Figure

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

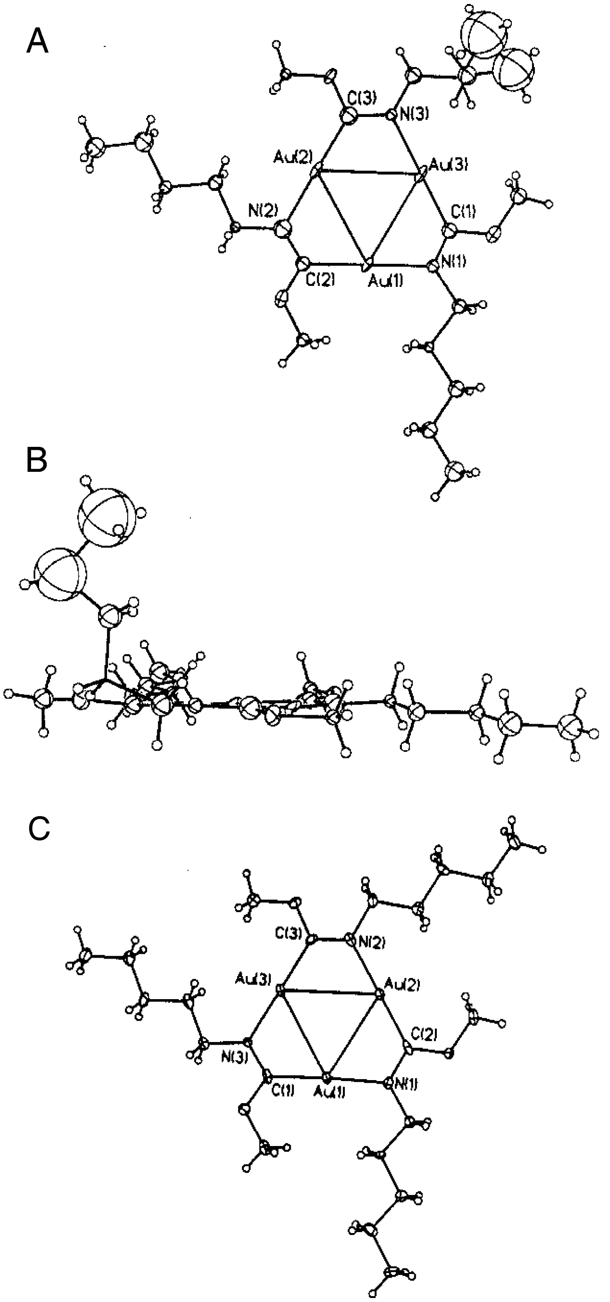

Figure 5. (A and B) Drawings of the molecular structure of $Au^I_3(n\text{-}PentN{=}COMe)_3$ in the orthorhombic polymorph. (C) View of one of the four molecules of $Au^I_3(n\text{-}PentN{=}COMe)_3$ in the triclinic polymorph. The other three molecules in the asymmetric unit of the triclinic polymorph have similar structures.

5 shows a drawing of one of these molecules. The interatomic distances and angles for the central nine-membered rings in these different molecules are similar, as can be seen from the data in Table 2.

The packing pattern of the four independent molecules in the triclinic polymorph is shown in Figure 7. Again, only the positions of the gold atoms are shown. Each of the four independent molecules interacts with two adjacent molecules through Au···Au contacts that range in distance from 3.3258(6) to 3.8125(6) Å.

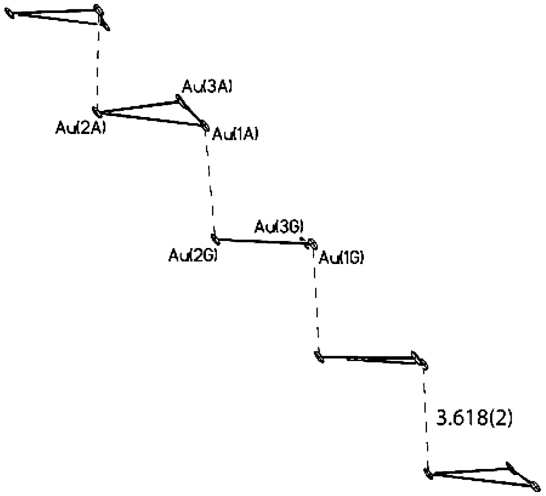

Figure 6. View of the interactions between molecules in the orthorhombic polymorph of $Au^I_3(n\text{-}PentN{=}COMe)_3$. Only the positions of the gold atoms are shown.

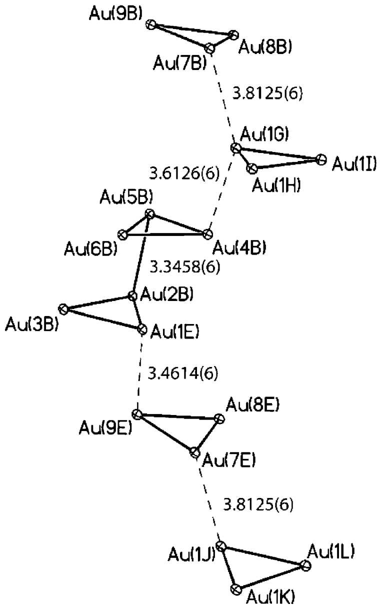

Figure 7. Drawing showing the intermolecular contacts in the triclinic polymorph of $Au^I_3(n\text{-}PentN{=}COMe)_3$. Only the positions of the gold atoms are shown.

Luminescence from the Polymorphs of $Au^I_3(n\text{-}PentN{=}COMe)_3$. Only the triclinic polymorph is luminescent at room temperature. The excitation and emission spectra for this polymorph are shown in Figure 8. The emission spectrum consists of a single emission at 654 nm, which is shifted further toward the red than any of the emissions seen for the polymorphs of $Au^I_3(MeN{=}COMe)_3$. In the excitation spectrum, the maximum occurs at 326 nm. Thus, there is a large Stokes shift in this spectrum. Consequently, the excited state is likely to have a significant geometric distortion.

The Structure of $Au^I_3(i\text{-}PrN{=}COMe)_3$. The asymmetric unit contains one molecule whose structure is shown in Figure 9. The methyl groups of the *i*-propyl groups lie above and below the plane of the molecule and, thereby, offer an impediment to self-association. As a result, the individual molecules of $Au^I_3(i\text{-}PrN{=}COMe)_3$ are well separated in the solid, as shown in the stereo diagram in Figure 10. In this case, the closest contact between gold atoms is 6.417 Å.

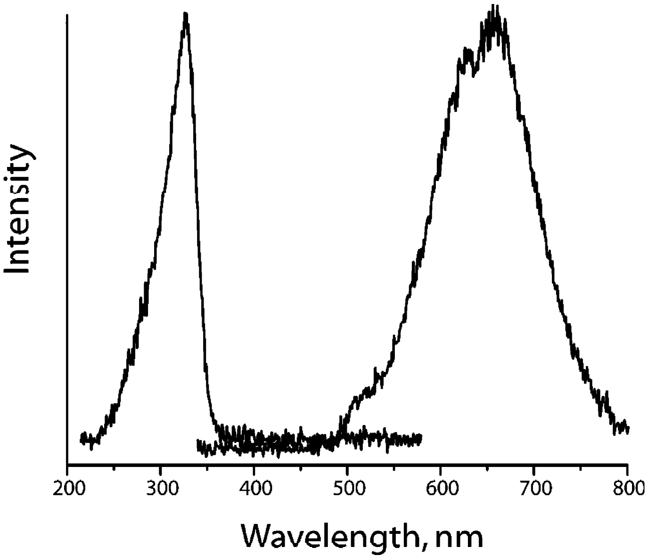

Figure 8. Emission and excitation spectra of the triclinic polymorph of Au^I_3(*n*-PentN═COMe)$_3$. No luminescence was detected from the orthorhombic polymorph.

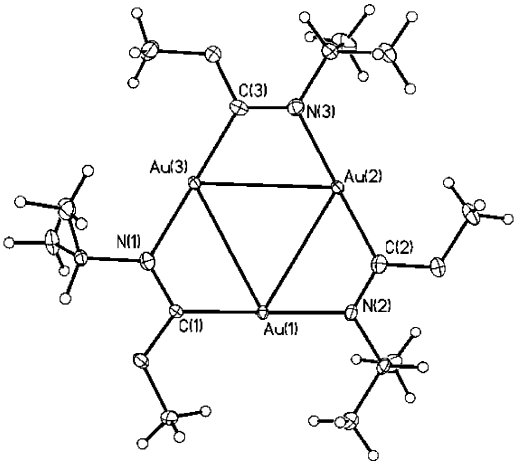

Figure 9. Molecular structure of Au^I_3(*i*-PrN═COMe)$_3$.

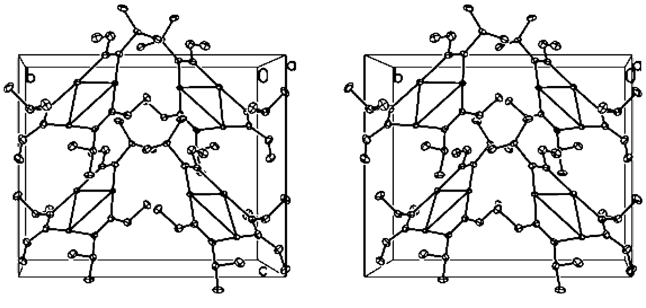

Figure 10. Stereo drawing showing the packing of molecules of Au^I_3(*i*-PrN═COMe)$_3$. The closest Au···Au contact is long at 6.417 Å.

Thus, there are no aurophilic interactions between the trimeric molecules in this solid.

Crystals of Au^I_3(*i*-PrN═COMe)$_3$ do not luminesce at 298 K.

Discussion

This work presents new examples of polymorphs of gold compounds in which the nature of the aurophilic interactions between two-coordinate gold(I) centers differ. These are true polymorphs and do not involve the inclusion of any solvent molecules in the crystals. For Au^I_3(MeN═COMe)$_3$, three polymorphs have been characterized, while two polymorphs of Au^I_3(*n*-PentN═COMe)$_3$ have been identified. For Au^I_3(MeN═COMe)$_3$, the principle difference among the three polymorphs involves the nature of the relative disposition of the molecules with respect to each other. The hexagonal and monoclinic polymorphs of Au^I_3(MeN═COMe)$_3$ contain prismatic stacks of molecules that use structural motif **C** in Chart 2. In the case of the hexagonal polymorph, these stacks are infinite, while in the monoclinic polymorph, the stack consists of only three molecules. Related, but slightly twisted, prismatic arrangements of pairs of the trimers are present in the charge-transfer adducts, {Au_3(MeN═COEt)$_3$}$_2$•2,7-dinitro-9-fluorenone and {Au_3(MeN═COEt)$_3$}$_2$•2,4,7-trinitro-9-fluorenone.[5] The hexagonal polymorph of Au^I_3(MeN═COMe)$_3$ also contains offset stacks involving structural motif **D**, which are not found in either of the other two polymorphs of this compound. The triclinic polymorph has a combination of motifs **A** and **B**.

In contrast, the two polymorphs of Au^I_3(*n*-PentN═COMe)$_3$ differ not only in the relative positions of the individual molecules but also in the disposition of peripheral substituents. In the needles of the orthorhombic polymorph, one of the *n*-Pent substituents protrudes so that it extends nearly perpendicular to the plane of the nine-membered ring. This substituent displays a high degree of thermal motion. Although there are four independent molecules in the asymmetric unit of the triclinic polymorph of Au^I_3(*n*-PentN═COMe)$_3$, these have very similar structures with all of the peripheral substituents lying near the plane of the nine-membered ring at the cores of the trimers. The four independent molecules in the triclinic polymorph are arranged so that the closest Au···Au contacts range from 3.3258(6) to 3.8125(6) Å, as shown in Figure 7. In this arrangement, pairs of trimers interact through a single aurophilic interaction so that the structural motif shown as **A** is used. In the orthorhombic polymorph, the molecules are arranged in a stair-step fashion using structural motif **A**, but here, the closest Au···Au contact is rather long, 3.618(2) Å.

Only the triclinic polymorph of Au^I_3(*n*-PentN═COMe)$_3$ is luminescent, and it is tempting to associate this luminescence with the presence of the shorter Au···Au contacts between molecules in this polymorph. For example, such a correlation has been reported for $[Au(SCN)_2]^-$ in salts with different cations.[17]

Within crystals of Au^I_3(*i*-PrN═COMe)$_3$, the individual molecules are widely separated, and these crystals are nonluminescent. This observation is consistent with our suggestion that the room-temperature luminescence seen for trinuclear complexes of this type originates from the aurophilic interactions between molecules.

Chart 3 shows several other types of trimeric gold(I) complexes, **1**,[18,19] **2**,[20] and **3**,[21,22] which have molecular

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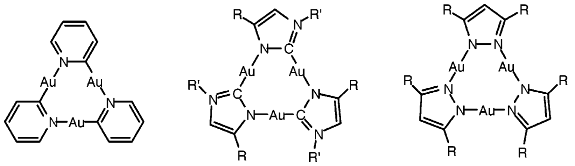
(17) Coker, N. L.; Krause Bauer, J. A.; Elder, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 12.

Chart 3



1 2 3

structures that are similar to $Au^I_3(MeN{=}COMe)_3$.[23] These complexes all involve linear two-coordinated gold ions that are connected by bridging ligands to form nearly planar strain-free nine-membered rings. These trimers can pack in the solid state in a variety of different motifs that frequently involve some degree of Au(I)···Au(I) interaction. Thus, $Au^I_3(MeC_6H_4N{=}COEt)_3$ packs as a pair of molecules using structural motif **B** with close intermolecular Au···Au contacts of 3.244(1) Å,[24] while $Au^I_3(MeOC{=}NCH_2Ph)_3$ crystallizes with no significant aurophilic interactions between the trimers.[16] In the latter, the closest intermolecular Au···Au contact is 3.662 Å. The packing motifs of the molecules shown in Chart 3 can be quite complex. For example, $Au^I_3(NC_5H_4)_3$, **1**, crystallizes with two different structural arrangements: dimers that utilize structural motif **B** and extended offset chains that utilize motifs **A** and **B** to connect alternating pairs of molecules.[18] Raptis and co-workers found that **2** with R = H and R′ = Me crystallizes with 15 different molecules in the asymmetric unit.[25] Five of these molecules are independent with no intermolecular Au···Au interactions, while two of them form a slightly twisted prismatic dimer that uses structural motif **C**. Similar arrangements are found 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.[5] The remaining eight molecules along with a second symmetry-related set of eight molecules form an aggregate of 16 molecules joined by aurophilic interactions at distances less than 3.6 Å with connections involving structural motifs **A** and **B**.

However, none of these other trinuclear complexes have been found to display the infinite prismatic stacking with extended Au(I)···Au(I) interactions that is characteristic of the hexagonal polymorph of $Au^I_3(MeN{=}COMe)_3$, and none show the offset and disordered stacks that are also present in this polymorph. The compact nature of $Au^I_3(MeN{=}COMe)_3$, which lacks protruding peripheral substituents, contributes to the ability of this molecule to pack with multiple degrees of disorder in the hexagonal polymorph. Energy storage in this polymorph is likely to involve charge separation with charge trapping involving particular sites that are provided by the disorder present within this unusual polymorph.[2,3] The results presented here on the newly identified polymorphs of $Au^I_3(MeN{=}COMe)_3$ reinforce our initial premise that the solid-state structure of the hexagonal polymorph of $Au^I_3(MeN{=}COMe)_3$ is crucial to the observation of solvoluminescence. These new polymorphs lack the extended structures using motifs **C** and **D** that are present in the hexagonal form. They also lack the long-lived low-energy emission that is involved in solvoluminescence.

Experimental Section

Materials. Isocyanides are toxic, foul smelling, and need to be handled appropriately. Methyl isocyanide was prepared by a known route.[26] Samples of *n*-pentyl isocyanide and *i*-propyl isocyanide were purchased from Aldrich and used as received. Chloro(triphenylarsine)gold(I) was prepared by a method adapted from the synthesis of chloro(triphenylphosphine)gold(I).[27] A previously reported procedure was used for the preparation of $Au^I_3(MeN{=}COMe)_3$.[1] All reactions were carried out in the atmosphere at room temperature in a well-ventilated hood.

$Au^I_3(MeN{=}COMe)_3$. A previously reported procedure was used for the preparation of $Au^I_3(MeN{=}COMe)_3$.[1] Colorless crystals of the triclinic polymorph were obtained by evaporation of a dichloromethane solution of the complex. Crystals of the monoclinic polymorph with a blue luminescence can be obtained by layering diethyl ether over a dichloromethane solution of the complex. The data reported here were collected on a sample of $Au^I_3(MeN{=}COMe\text{-}d_3)_3$ that was obtained using methanol-d_3 in the synthesis. We have confirmed that $Au^I_3(MeN{=}COMe\text{-}d_3)_3$ forms both the hexagonal and monoclinic polymorphs, and we do not attribute any major effects to the presence of deuterium in the sample.

Au^I_3(*n*-PentN=COMe)$_3$. A 255.1 mg (0.464 mmol) sample of $(Ph_3As)Au^ICl$ was suspended in 10 mL of methanol. A saturated methanolic solution of potassium hydroxide (41.2 mg, 0.734 mmol) was added to the mixture, followed by the dropwise addition of 0.50 mmol of *n*-pentyl isocyanide. Once the isocyanide was added to the solution, the solid dissolved. However, immediately after the dissolution of the solid, a new colorless precipitate formed. The resulting slurry was stirred for 3 h. The solid product was removed by filtration and washed with methanol. The solid was dissolved in diethyl ether, and the solution was filtered. Slow evaporation of the solvent produced a mixture of crystals of Au^I_3(*n*-PentN=COMe)$_3$ with two clearly different morphologies: needles of the orthorhombic polymorph and blocks of the triclinic polymorph. mp 78 °C. IR spectrum for the orthorhombic needles: ν(C=N) 1537.0, 1486.8, 1442.5, 1402.0, 1363.4, 1321.0, 1286.3, 1255.4, 1172.5 cm^{-1}. ^1H NMR of the triclinic blocks in chloroform-*d*: 3.995 s (3H, OMe), 3.413 t (2H, NCH_2), 1.689 m (2H), 1.41 (br m, 4H), 0.889 t (3H, CH_3). ^1H NMR of the orthorhombic needles in chloroform-*d*: 3.993 (s, OMe), 3.420 (t, NCH_2), 1.710 (m), 1.32 (br m), 0.874 (t, CH_3).

Au^I_3(*i*-PrN=COMe)$_3$. The same synthetic procedure was used as described above for the preparation of Au^I_3(*n*-PentN=COMe)$_3$. However, once the gold precursor dissolved, the solution remained clear and a solid never formed. Therefore, the methanolic solution was stirred for 6 h, filtered, and loosely capped with a rubber septum. Within 2 days, after the evaporation of a slight amount of methanol, large colorless crystals formed. mp 159−160 °C. IR

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spectrum: ν(C=N) 2962.1, 2929.3, 2831.0, 1531.2, 1452.1, 1429,0, 1375.0, 1359.6, 1211.1, 1147.4, 1120.4, 1051.0 cm^{-1}. ^{1}H NMR in chloroform-*d*: 4.021 (s, 3H, OMe), 4.670 (heptet, 1H, CH), 1.162 (d, 6H, CH_3).

X-ray Crystallography and Data Collection. The crystals were removed from the source together with a small amount of mother liquor and immediately coated with a hydrocarbon oil on the microscope slide. A suitable crystal of each compound was mounted on a glass fiber with silicon grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo Kα radiation. No decay was observed in 50 duplicate frames at the end of each data collection. Crystal data are given in Table 1.

The structures were solved by direct methods and refined using all data (based on F^2) using SHELXTL 5.1 software. A multiscan method utilizing equivalents was employed to correct for absorption.[28] Hydrogen atoms were added geometrically and refined with a riding model.

Physical Measurements. Infrared spectra were recorded as pressed KBr pellets on a Matteson Galaxie Series FTIR 3000 spectrometer. Electronic absorption spectra were recorded using a Hewlett-Packard 8450A diode array spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Jobin Yvon Fluoromax-P luminescence spectrophotometer.

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Supporting Information Available: X-ray crystallographic files in CIF format for the triclinic and monoclinic polymorphs of $Au^I_3(MeN{=}COMe)_3$, the orthorhombic and triclinic polymorphs of Au^I_3(*n*-PentN=COMe)$_3$, and Au^I_3(*i*-PrN=COMe)$_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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