

# Aurophilic Interactions in Cationic Gold Complexes with Two Isocyanide Ligands. Polymorphic Yellow and Colorless Forms of [(Cyclohexyl Isocyanide)<sub>2</sub>Au<sup>+</sup>](PF<sub>6</sub>)<sup>-</sup> with Distinct Luminescence

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**Abstract:** Crystallographic studies of yellow and colorless forms of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>+</sup>](PF<sub>6</sub>)<sup>-</sup> show that they are polymorphs with differing, but close, contacts between the gold atoms which form extended chains. In the colorless polymorph the gold cations form linear chains with a short Au...Au contact (3.1822(3) Å) indicative of an aurophilic attraction. The structure of the yellow polymorph is more complicated with four independent cations forming kinked, slightly helical chains with very short Au...Au contacts of 2.9803(6), 2.9790(6), 2.9651(6), and 2.9643(6) Å. However, in the related compound, [(CH<sub>3</sub>NC)<sub>2</sub>Au<sup>+</sup>](PF<sub>6</sub>)<sup>-</sup>, each cation is surrounded by six hexafluorophosphate ions and there is no close Au...Au contact despite the fact that the isocyanide ligand has less steric bulk. The crystalline colorless and yellow polymorphs are both luminescent at 298 K, λ<sub>max</sub>: 424 nm (colorless) or 480 nm (yellow). Colorless solutions of the two polymorphs have identical absorption spectra and are nonluminescent at room temperature. Freezing solutions of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>+</sup>](PF<sub>6</sub>)<sup>-</sup> produces intense luminescence which varies depending upon the solvent involved. Each polymorph melts to give a colorless but luminescent liquid which reverts to the yellow polymorph upon cooling.

## Introduction

In the solid state, uncharged, colorless Au(I) complexes show a pronounced propensity to self-associate. Attractive aurophilic interactions occur between closed shell, two-coordinate Au(I) complexes when the Au...Au separations are less than 3.6 Å<sup>1-3</sup> and are important in determining the solid-state structures of many of these complexes.<sup>4,5</sup> Theoretical studies have shown that this weakly bonding interaction is the result of correlation effects that are enhanced by relativistic effects.<sup>6-9</sup> Experimental studies have shown that the strength of this attractive interaction is comparable to hydrogen bonding: i.e. ca. 7–11 kcal/mol.<sup>10,11</sup> Aurophilic attractions have been implicated in several luminescent features of gold(I) complexes,<sup>12</sup> including emission from

dimers,<sup>13</sup> solvoluminescence,<sup>14</sup> luminescence from [Au(CN)<sub>2</sub>]<sup>-</sup> in a variety of environments,<sup>15</sup> solvate dependent emission from the dimer, {Au(S<sub>2</sub>CN(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>)<sub>2</sub>},<sup>16</sup> and a potassium ion sensor.<sup>17</sup> NMR studies have shown that aurophilic attractions persist in solution where they are favored by high concentrations and low temperatures.<sup>18</sup>

Recently we found that the colorless, cationic gold carbene complex, [Au{C(NHCH<sub>3</sub>)<sub>2</sub>}]<sup>+</sup>(PF<sub>6</sub>)<sup>-</sup>, undergoes aggregation through aurophilic attraction in the solid state and in frozen solutions.<sup>19</sup> In the crystalline state, the aurophilic attraction and hydrogen bonding among ligand N–H groups and the hexafluoro-

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rophosphate ions helps to overcome the inherent Coulombic repulsion between cations to produce extended columns of cations with an Au...Au separation of only 3.1882(1) Å. These crystals are strongly luminescent, but when dissolved in solution, the salt is no longer luminescent. However, aggregation of these cations occurs upon freezing of the solvents and produces some notable variations in the luminescence that are readily detected by the human eye. Thus, the frozen acetonitrile solution produces a green-yellow luminescence, while in dimethyl sulfoxide and pyridine the emission is different shades of blue, and with acetone it is orange. However, in frozen dimethylformamide no luminescence is observed from this complex. These variations in luminescence have been ascribed to the formation of aggregates of cations which self-associate through aurophilic attractions. With other anions the nature of the self-association differs,<sup>19</sup> and discrete dimers of [Au{C(NHCH<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sup>+</sup> have been isolated.<sup>20</sup>

However, such self-association through aurophilic interactions appears to be lacking in some related salts. Specifically, a study by Schmidbaur and co-workers on the colorless bis(isocyanide)-gold(I) complexes, [(RNC)<sub>2</sub>Au<sup>I</sup>]X, with R = methyl, phenyl, and mesityl and X = triflate or tetrafluoroborate, found that supramolecular aggregation is observed only with the smallest alkyl substituent.<sup>21</sup> Moreover, the Au...Au interaction in [(CH<sub>3</sub>NC)<sub>2</sub>Au<sup>I</sup>](O<sub>3</sub>SCF<sub>3</sub>) is quite long, 3.624 Å. In view of the unusual spectroscopic studies of the gold carbene complexes and the lack of aurophilic attractions in the isocyanide gold cations, we became interested in the observation of a *yellow* gold complex which was reported to form during the preparation of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>).<sup>22</sup>

## Results

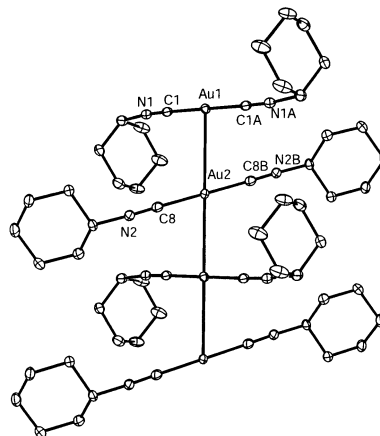
The two forms of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) (colorless and yellow) were synthesized using previously reported methods.<sup>22</sup> Yellow crystals suitable for X-ray diffraction were taken directly from the reaction mixture. The colorless polymorph was obtained by dissolving the yellow form in hot 1-propanol and allowing the solution to slowly cool to room temperature and to gradually evaporate. Crystallographic data for the two polymorphs are given in Table 1. These data indicate that the yellow and colorless forms of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) are true polymorphs (different crystalline forms of the same molecule or in this case salt),<sup>23,24</sup> and neither involves the inclusion of any solvent molecules into the solid.

**Crystal Structure of the Colorless Polymorph, [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>).** A perspective view of a portion of the structure of the colorless polymorph of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) is shown in Figure 1. Selected bond lengths and angles are given in the figure caption. The asymmetric unit of the colorless polymorph consists of two half-cations with the gold atoms located at centers of symmetry and one anion in a general position. Since each gold atom is located on a center of symmetry, the two isocyanide ligands coordinate gold in a linear fashion. In the cation containing Au1, the isocyano group is

**Table 1.** Crystallographic Data for Compounds 1–3

	[(C <sub>6</sub> H <sub>11</sub> NC) <sub>2</sub> Au <sup>I</sup> ](PF <sub>6</sub> )		[(MeNC) <sub>2</sub> Au <sup>I</sup> ](PF <sub>6</sub> )
	colorless polymorph	yellow polymorph	
color/habit	colorless needle	yellow plate	colorless block
formula	C <sub>14</sub> H <sub>22</sub> AuF <sub>6</sub> N <sub>2</sub> P	C <sub>14</sub> H <sub>22</sub> AuF <sub>6</sub> N <sub>2</sub> P	C <sub>4</sub> H <sub>6</sub> AuF <sub>6</sub> N <sub>2</sub> P
fw	560.27	560.27	424.04
<i>a</i> , Å	6.3644(5)	11.5235(7)	9.8097(7)
<i>b</i> , Å	16.9806(15)	24.1416(15)	9.8097(7)
<i>c</i> , Å	16.7224(13)	26.0516(16)	9.8097(7)
α, deg	90	90	90
β, deg	92.693(3)	90	90
γ, deg	90	90	90
<i>V</i> , Å <sup>3</sup>	1805.2(3)	7247.4(8)	943.99(12)
<i>Z</i>	4	16	4
cryst syst	monoclinic	orthorhombic	cubic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Pa
<i>T</i> , °C	91(2)	91(2)	90(2)
λ, Å	0.710 73	0.710 73	0.710 73
ρ, g/cm <sup>3</sup>	2.061	2.054	2.984
μ, cm <sup>-1</sup>	8.294	8.264	15.809
<i>R</i> 1 (obsd data) <sup>a</sup>	0.019	0.055	0.036
w <i>R</i> 2 <sup>a</sup> (all data, <i>F</i> <sup>2</sup> refinement)	0.053	0.123	0.075

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



**Figure 1.** View of a chain of cations within the colorless polymorph of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>). The Au1...Au2 distance is 3.1822(3) Å (1/2 of *a*). Anions are deleted for clarity. Selected distances: Au1–C1, 1.973(2); Au2–C8, 1.975(2); C1–N1, 1.134(3); C8–N2, 1.136(3) Å. Selected angles: Au1–Au2–Au1', Au2–Au1–Au2', 180; Au1–C1–N1, 178.3(2); Au2–C8–N2, 177.6(2)°.

located in an axial site on the cyclohexyl ring, while in the cation containing Au2, the isocyano group resides in an equatorial position in the cyclohexyl ring. The gold cations aggregate into an infinite linear chain along the crystallographic *a* axis. Within these chains, the Au...Au contact (3.1822(3) Å) is indicative of an aurophilic attraction between cations. Adjacent cations alternate in orientation and form a semi-staggered array with a dihedral C1–Au1–Au2–C8 angle of 65.9°.

Figure 2 shows a stereoscopic view of two chains of the cations and allows the reader to see the location of the anions. The closest approach of a fluorine atom of a hexafluorophosphate ion to a gold atom is 3.070 Å for Au1...F4. This distance is similar to the sum of the van der Waals radii for Au and F (3.13 Å).

**Crystal Structure of the Yellow Polymorph, [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>).** Figure 3 shows a drawing of a portion of the structure of the yellow polymorph of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>). This structure is more complicated than that of the

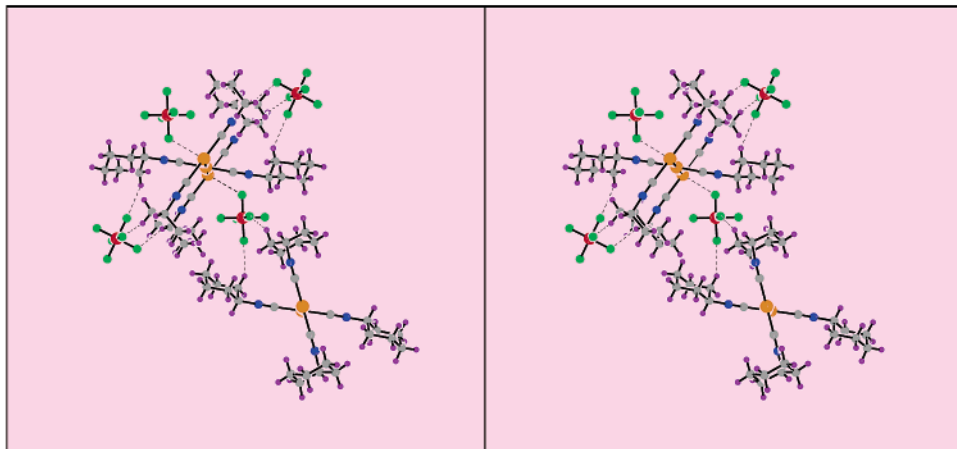
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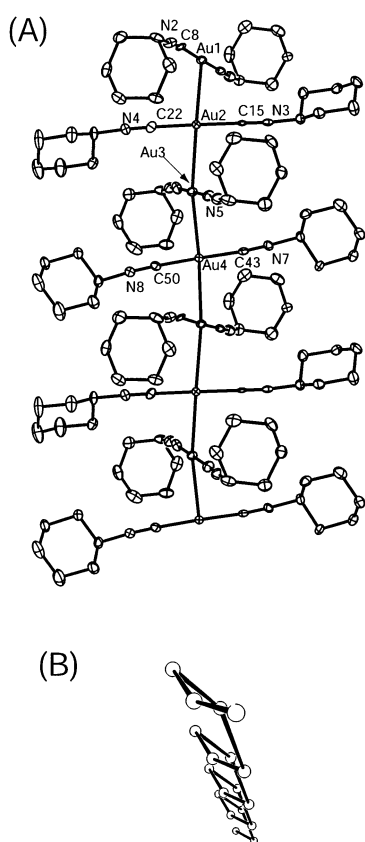
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**Figure 2.** Stereoview of a two chains of gold ions and the hexafluorophosphate ions in the colorless polymorph of  $[(C_6H_{11}NC)_2Au^+](PF_6)$ . Atom colors are as follows: gold, orange; fluorine, green; phosphorus, red; carbon, gray; hydrogen, purple; nitrogen, blue.



**Figure 3.** (A) View of a chain of cations within the yellow polymorph of  $[(C_6H_{11}NC)_2Au^+](PF_6)$ . The  $Au\cdots Au$  distances are as follows:  $Au1-Au2$ , 2.9803(6);  $Au1-Au4'$ , 2.9790(6);  $Au2-Au3$ , 2.9651(6); and  $Au3-Au4$ , 2.9643(6) Å. Anions are deleted for clarity. Other selected distances:  $Au1-C1$ , 1.974(9);  $Au1-C8$ , 2.007(9);  $Au2-C15$ , 1.993(9);  $Au2-C22$ , 1.972(10);  $Au3-C29$ , 1.965(11);  $Au3-C36$ , 1.985(11);  $Au4-C50$ , 1.961(10);  $Au4-C43$ , 1.986(9);  $C1-N1$ , 1.136(13);  $C8-N2$ , 1.108(13);  $C15-N3$ , 1.123(11);  $C22-N4$ , 1.140(12);  $C29-N5$ , 1.145(14);  $C36-N6$ , 1.129(14);  $C43-N7$ , 1.131(12);  $C50-N8$ , 1.173(12) Å. Selected angles:  $Au4'-Au1-Au2$ , 173.313(18);  $Au1-Au2-Au3$ , 152.129(17);  $Au2-Au3-Au4$ , 169.652(18);  $Au1'-Au4-Au3$ , 153.637(18);  $C1-Au1-C8$ , 177.8(4);  $C15-Au2-C22$ , 176.8(4);  $C29-Au3-C36$ , 179.8(5);  $C43-Au4-C50$ , 178.0(4);  $Au1-C1-N1$ , 176.0(10);  $Au1-C8-N2$ , 171.4(9);  $Au2-C15-N3$ , 175.2(9);  $Au2-C22-N4$ , 174.9(10);  $Au3-C29-N5$ , 178.7(11);  $Au3-C36-N6$ , 174.2(11);  $Au4-C43-N7$ , 175.6(9);  $Au4-C50-N8$ , 177.1(9). (B) View down a chain of gold ions (with all other atoms deleted) which emphasizes the helical nature of the chain.

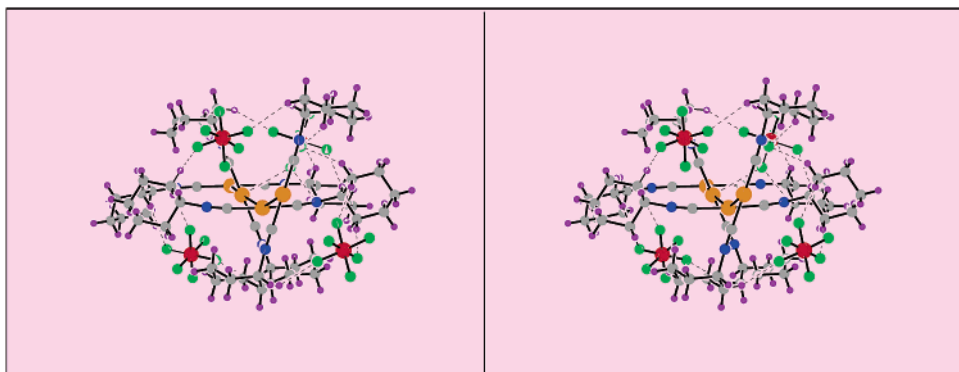
colorless polymorph, since it contains four cations and four

anions in the asymmetric unit. Each of the four individual cations involves a central gold ion which is coordinated in a linear fashion by the two isocyanide ligands. The isocyano groups in the cations containing  $Au1$  and  $Au3$  are in axial positions in the cyclohexyl rings, while the isocyano groups in the cations containing  $Au2$  and  $Au4$  are in equatorial positions of the cyclohexyl rings. These positions are probably determined by crystal packing forces. The cations form infinite chains through aurophilic interactions. Within these kinked chains, the cations stack with the ligands in semi-staggered fashions. Although bulky cyclohexyl groups are present, the longest  $Au\cdots Au$  distance (2.9803(6) Å) is on the short end of aurophilic attractions and is much shorter than the corresponding distances in the colorless polymorph (3.1822(3) Å) and in  $[Au\{C(NHCH_3)_2\}_2](PF_6)\cdot 0.5$ acetone (3.1882(1) Å).<sup>19</sup> The other three  $Au\cdots Au$  distances (2.9790(6), 2.9651(6), and 2.9643(6) Å) approach the  $Au\cdots Au$  distance in metallic gold (2.889(1) Å). The chain of cations is bent, with  $Au\cdots Au\cdots Au$  angles of 173.313(18), 152.129(17), 169.652(18), and 153.637(18)°. All eight independent cyclohexyl rings adopt the chair conformation.

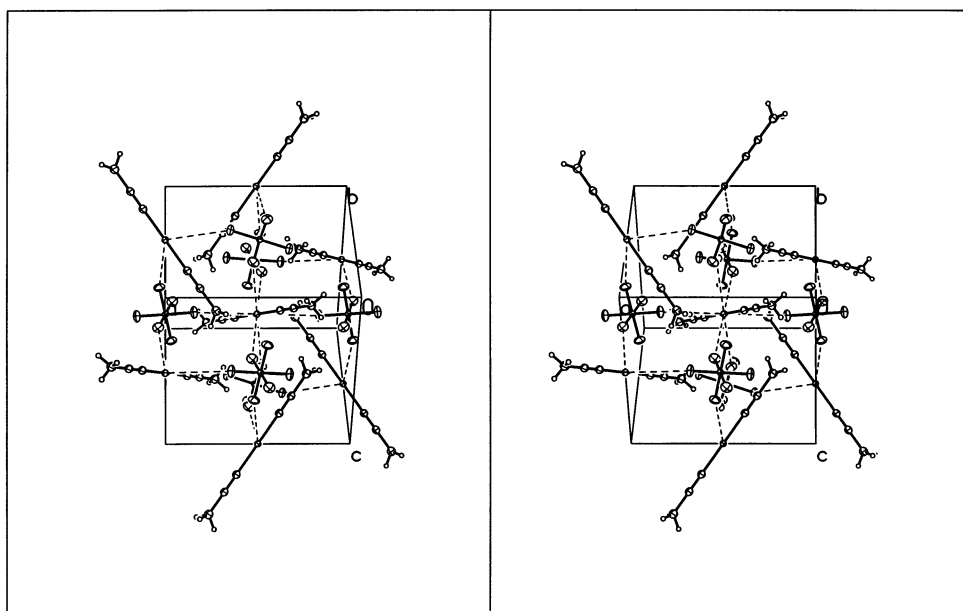
The anions are nestled in space between the staggered cyclohexyl isocyanide ligands. Three of the four hexafluorophosphate anions are disordered with two sets of alternate positions for the fluorine atoms. Figure 4 shows the positioning of the most prevalent of the hexafluorophosphate sites within the kinked chains of gold atoms. The closest approach that a hexafluorophosphate ion makes with the cation involves a fluorine to gold contact ( $Au3\cdots F7$ , 3.152 Å) whose magnitude is close to the sum of the van der Waals radii (3.13 Å) for these two atoms. The other close anion/cation interactions involve short  $F\cdots H$  contacts.

The yellow polymorph of  $[(C_6H_{11}NC)_2Au^+](PF_6)$  crystallizes in the chiral space group  $P2_12_12_1$ . As a consequence, the chains of gold atoms form a helical ribbon as shown in part B of Figure 3. However, the structure itself was refined as a racemic twin with a Flack twin parameter of 0.5. Consequently due to the twinning, the crystal consists of a racemic mixture of the two enantiomers of the helical chains.

**Crystal Structure of Colorless  $[(CH_3NC)_2Au^+](PF_6)$ .** To see whether the hexafluorophosphate ion is responsible in some fashion for the close approach of the Au(I) centers in the polymorphs of  $[(C_6H_{11}NC)_2Au^+](PF_6)$ , the structure of  $[(CH_3-$



**Figure 4.** Stereoview of a chain of cations and the hexafluorophosphate ions in the yellow polymorph of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ . Atom colors are as follows: gold, orange; fluorine, green; phosphorus, red; carbon, gray; hydrogen, purple; nitrogen, blue.



**Figure 5.** View of the unit cell of  $[(CH_3NC)_2Au^I](PF_6)$ . The shortest gold/gold separation is  $6.9365(5)$  Å, and the closest Au/F contact is  $3.411(4)$  Å. Selected distances: Au1–C1,  $1.987(12)$ ; C1–N1,  $1.128(16)$  Å. Selected angles: C1–Au–C',  $180$ ; Au–C1–N1,  $180^\circ$ .

$NC)_2Au^I](PF_6)$  was determined to provide a comparison with the previously obtained structure of  $[(CH_3NC)_2Au^I](O_3SCF_3)$ .<sup>21</sup> A view of the unit cell of  $[(CH_3NC)_2Au^I](PF_6)$  is shown in Figure 5. Each cation has crystallographic  $\bar{3}$  symmetry with the crystallographic axis passing through the CNCAuCNC portion of the cation. Dimensions within the cation are entirely normal.

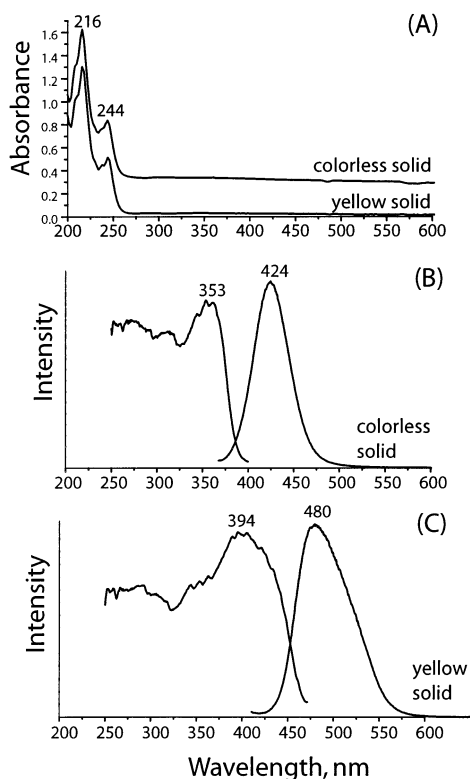
The closest approach of two neighboring  $Au^I$  centers is  $6.9365(5)$  Å, which is much longer than the closest  $Au \cdots Au$  contact ( $3.624$  Å) in  $[(CH_3NC)_2Au^I](O_3SCF_3)$  and far too long for any aurophilic interaction. Moreover, in  $[(CH_3NC)_2Au^I](PF_6)$  each cation is surrounded by six hexafluorophosphate ions with the shortest Au/F contact being  $3.411(4)$  Å, which is longer than the sum of the van der Waals radii ( $3.13$  Å) of gold and fluorine. Thus, the hexafluorophosphate ion alone does not promote aurophilic interactions.

**Absorption and Emission Spectra of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  and  $[(CH_3NC)_2Au^I](PF_6)$ .** As seen in part A of Figure 6, the absorption spectra for acetonitrile solutions of the two forms of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  are identical, with prominent  $\lambda_{max}$  at 244 and 216 nm. Thus, the absorption data show that the differences between the two forms do not persist in solution and are consistent with the proposition that these salts are truly

polymorphs. Indeed these spectra are also virtually identical to the spectrum reported for  $[(EtNC)_2Au^I](ClO_4)$  earlier.<sup>25</sup> The absorption and magnetic circular dichroism spectra for  $[(EtNC)_2Au^I](ClO_4)$  have been interpreted as resulting from metal-to-ligand charge-transfer states that involve excitation from the filled gold  $d_{z^2}$  orbital to a  $\pi^*$  orbital of the ligand.<sup>25</sup> Since the identity of the alkyl substituent on the isocyanide has little effect on the  $\pi^*$  orbital, which is localized within the isocyano function, the absorption spectra of the different alkylisocyanide complexes of the type  $[(RNC)_2Au^I]^+$  are similar. Thus, the absorption spectrum of  $[(CH_3NC)_2Au^I](PF_6)$  is also similar to that of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  with corresponding absorption maxima at 246 and 214 nm. At room temperature, solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  or  $[(CH_3NC)_2Au^I](PF_6)$  are nonluminescent.

However, each of the two crystalline polymorphs displays a distinct luminescence spectrum. Relevant data are shown in parts B and C of Figure 6. Visually, the colorless polymorph produces a bluish-white emission. Its emission spectrum at 298 K displays a maximum at 424 nm with an excitation maximum at 353 nm.

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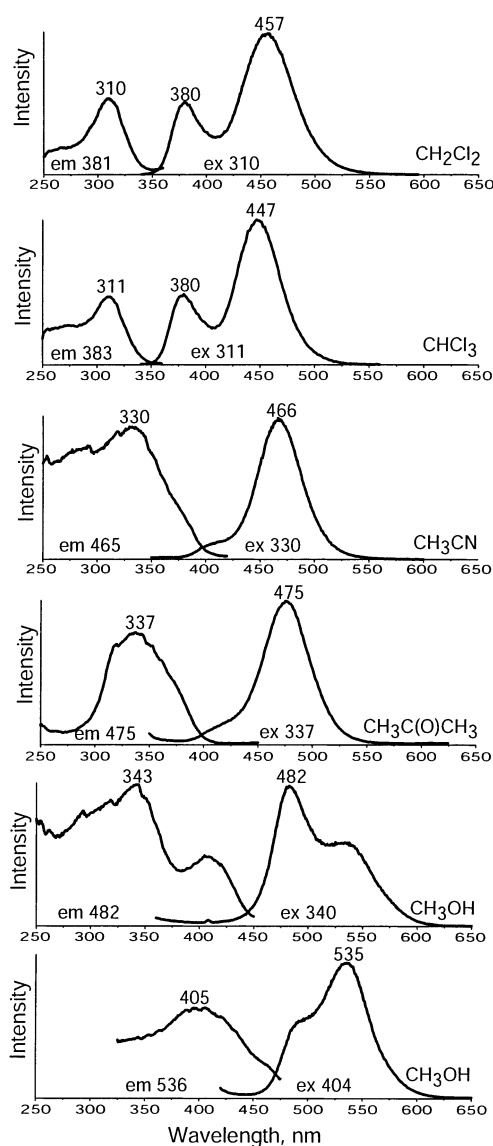


**Figure 6.** (A) The absorption spectra of acetonitrile solutions of the yellow (lower) and the colorless (upper, offset by 0.4 absorbance units) polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ . The emission (right side) and excitation (left side) spectra of (B) the colorless and (C) the yellow polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ .

The yellow polymorph visually produces a yellow-green luminescence. The emission spectrum shows emission at a longer wavelength (480 nm) than the colorless polymorph and an excitation profile with a peak at 394 nm. The yellow polymorph, as expected from its color, has an excitation maximum at lower energy (394 nm) than does the colorless polymorph (353 nm). Notice, however, that for each of the two polymorphs the onset of the excitation profile occurs at a longer wavelength than that seen in the absorption spectrum (part A of Figure 6). Consequently, the luminescence must result from the extended  $Au\cdots Au$  interactions between cations in their solid-state supramolecular structures. The emission lifetimes of the two polymorphs are similar. The yellow polymorph shows a long-lived emission with a lifetime of  $0.73 \mu s$ , while the lifetime for the emission from the colorless polymorph is  $0.55 \mu s$ . These lifetimes suggest that the emission is due to phosphorescence.

In contrast to the behavior of the polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ , crystalline  $[(CH_3NC)_2Au^I](PF_6)$ , which lacks auophilic interactions, is not luminescent. Hence, it provides further confirmation of the connection between  $Au\cdots Au$  interactions and the luminescence of these gold(I) complexes.

The absorption spectra of both crystalline polymorphs have been examined in KBr wafers. The colorless polymorph displays an absorption maxima at 340 nm, which is similar to the excitation maxima at 353 nm seen in Figure 5. The yellow polymorph has an absorption maxima at 400 nm, which corresponds to the excitation maximum at 394 nm. The absorption maxima at 340 nm in the white polymorph and at 394 nm in the yellow polymorph are new features of the solid which do not have counterparts in the solution spectra shown

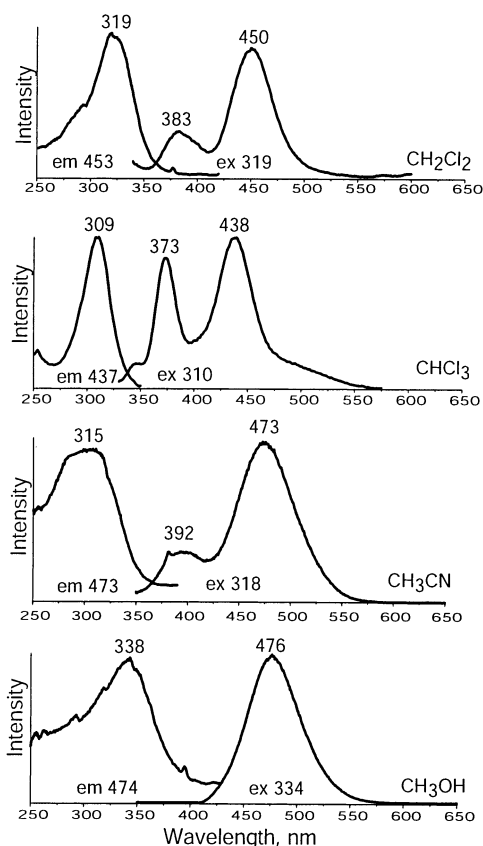


**Figure 7.** Emission (right) and excitation (left) spectra of frozen 6.0 mM solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  in various solvents at 77 K. The wavelength used to monitor the excitation profile is given below each excitation spectrum, and the wavelength used for excitation is shown below each emission spectrum.

in Figure 6. These additional features are believed to originate in the extended  $Au\cdots Au$  interactions and probably involve promotion of an electron from the filled  $5d_{z^2}$  band to the empty  $6p_z$  band where the  $z$  axis is collinear with the  $Au\cdots Au$  stacking direction.

While both polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  dissolve in a variety of organic solvents to give colorless, nonluminescent solutions, freezing these solutions does produce strong luminescence. Moreover, the emission spectra obtained from these frozen solutions vary as the solvent is changed. Visually the effect is not as striking as it is in the case of  $[Au\{C(NHCH_3)_2\}_2](PF_6)$ , but the emissions from these frozen solutions do show significant alterations, as seen in spectra shown in Figures 7 and 8.

Figure 7 presents emission and excitation spectra for 6.0 mM solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  in a variety of solvents which have been frozen at 77 K. The emission spectra from the frozen chloroform and dichloromethane solutions are similar with



**Figure 8.** Emission (right) and excitation (left) spectra of frozen 0.60 mM solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  in various solvents at 77 K. The wavelength used to monitor the excitation profile is given below each excitation spectrum, and the wavelength used for excitation is shown below each emission spectrum.

emission maxima at 380 and ca. 450 nm. The emission spectra from frozen acetone and acetonitrile solutions are also similar with a strong emission near 470 nm and a much weaker shoulder near 410 nm. The spectra obtained from frozen methanol solutions are quite different with emissions at 535 and 482 nm. The relative intensities of these two emission bands depend on the excitation wavelength with excitation at longer wavelengths producing enhanced emission at 535 nm.

Dilution of the solutions produces significant changes in the luminescence from some solutions. Figure 8 presents emission and excitation spectra for frozen 0.60 mM solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  at 77 K. The spectra obtained from chloroform and dichloromethane solutions are grossly similar to those shown in Figure 7. However, there are small changes in the band positions and in their relative intensities. The emission spectrum from the frozen acetonitrile solution is similar to that of the 6.0 mM solution seen in Figure 7 except for the increased intensity of the short wavelength band which is now at 392 nm. While the emission spectrum obtained from a 6.0 mM solution of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  in acetone resembled that of the corresponding spectrum obtained from frozen acetonitrile solution, no emission was detected from the frozen 0.60 mM acetone solution of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ . The emission from the frozen methanol solution seen in Figure 8 is markedly different from the spectra obtained from the more concentrated solution seen in Figure 7. The long wavelength emission at 535 nm is absent from the spectrum seen in Figure 8. The spectrum now shows a band at 476 nm which is similar to that seen in Figure 7.

**Infrared Spectroscopy.** The infrared spectra of the two polymorphs, each dispersed in a KBr wafer, have been examined. As might be expected, the two spectra are extremely similar. However, there are differences in the isocyanide stretching region. The colorless polymorph shows two bands in the  $\nu(CN)$  region at 2273 and 2256  $cm^{-1}$ , while the yellow polymorph shows a single band at 2257  $cm^{-1}$ .

**Thermal Behavior of the Polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ .** Heating the crystalline colorless polymorph results in melting over the range 115–120 °C to give a colorless melt. This melt is luminescent and produces a bluish-white emission that is visually similar to that from the crystalline colorless polymorph. Cooling of this melt, however, produces a luminescent yellow solid. The emission and excitation spectra of this solid are virtually identical to that of the yellow polymorph. Similar heating of the yellow polymorph reveals melting over the range 110–115 °C to produce a colorless melt which also produces a bluish-white emission. Cooling this melt produces a yellow solid with an emission and excitation spectrum indicative of the re-formation of the yellow polymorph. Since the colorless polymorph is transformed into the yellow polymorph in these experiments, the yellow polymorph must be the thermodynamically more stable form.

## Discussion

The results presented here demonstrate that  $[(C_6H_{11}NC)_2Au^I](PF_6)$  exists in two polymorphic forms each of which shows strong aurophilic attractions among the cations. The strong aurophilic attractions seen in both polymorphs contrast markedly with the structures of three other members of the  $[(RNC)_2Au^I]X$  family,  $[(CH_3NC)_2Au^I](PF_6)$ ,  $[(C_6H_5NC)_2Au^I](BF_4)$ , and  $[2,4,6-(CH_3)_3C_6H_2NC)_2Au^I](BF_4)$ , which have no aurophilic interactions, and  $[(CH_3NC)_2Au^I](O_3SCF_3)$ , which has only a weak interaction between cations ( $Au\cdots Au$  distances of 3.611 and 3.624 Å).<sup>21</sup> Although both forms of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  involve the formation of extended chains of cations, the  $Au\cdots Au$  separation in the yellow polymorph is significantly shorter than it is in the white polymorph. Additionally, the chain of cations in the yellow polymorph is slightly kinked into a helix, while it is crystallographically required to be linear in the white polymorph. To our knowledge, this represents the first case of polymorphism in gold(I) chain complexes where the polymorphs differ in the nature of the aurophilic attraction. However, since aurophilic interactions are relatively weak and can span such a wide range of  $Au\cdots Au$  distances, we suspect that further example of polymorphism involving varying degrees of aurophilic attraction will be found.

A closely related case of polymorphism in gold complexes involves the exceptionally interesting studies of Bowmaker and co-workers on  $\{(C_6H_{11})_3P\}_2AuBr$ .<sup>26</sup> This compound crystallizes as three polymorphs which differ not in the approach of one gold center to another but in the approach of the bromide ion to the gold center. Thus in the  $\alpha$  form, the cation is linear and the bromide ion is far from the gold at a distance of 3.764(4) Å. In the  $\beta$  form there are two molecules: one with a  $Au-Br$  distance of 2.894(1) Å and a slightly bent  $P-Au-P$  (162.06(9)°) portion; the other with a shorter  $Au-Br$  distance of 2.842(1) Å and a somewhat greater bend (157.71°) to the  $P-Au-P$  portion.

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In the  $\gamma$  polymorph the Au–Br distance is shorter yet (2.777(1) Å) and the P–Au–P portion is further bent (147.5(1)°). In contrast, although the colorless and yellow polymorphs of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) show significant differences in the environment of the gold ions, there is no bending of the C–Au–C portion of the cation that occurs as a result of the aurophilic attraction.

The structural variations seen in the polymorphs of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) and {(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>P}<sub>2</sub>AuBr are related to the concept of bond stretch isomers: molecules that “differ only in the length of one or several bonds”.<sup>27</sup> Several examples of bond stretch isomers have been identified,<sup>28</sup> and theoretical analyses of the phenomenon have been presented.<sup>29</sup> With regard to the variations seen in the Au···Au contacts in the yellow and colorless polymorphs of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>), these do not constitute bond stretch isomers in the strict sense of the definition, since the Au···Au interactions do not exist within a molecule or molecular ion but rather involve interionic interactions that do not persist in dilute solution. Nevertheless, significant differences must exist in the interionic interactions in the yellow and colorless polymorphs.

Two colorless polymorphs of {(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>As}AuCl have been reported.<sup>30</sup> These differ in the torsional angles of the phenyl groups and in molecular packing but do not have close Au···Au contacts. The shortest Au···Au separations are 5.916(1) Å for the needle modification or 6.913(1) Å for the prismatic modification. Both forms are luminescent, but the spectra of the two forms show only minor differences.<sup>31</sup> The luminescence arises from the triphenylarsine ligand  $\pi$ – $\pi$  states not from the metal centers.

Usually, the aurophilic interactions between monomeric, two-coordinate gold(I) complexes lead to simple dimerization rather than the formation of extended chains in which each gold center interacts with two neighbors. However, in the solid state {(Me<sub>2</sub>S)AuCl}<sub>n</sub> forms a bent chain structure with an Au···Au distance of 3.226(1) Å and an Au···Au···Au angle of 168.1(1)°.<sup>32</sup> Colorless {(2-picoline)AuCl}<sub>n</sub> forms a similar chain with an Au···Au distance of 3.1960(4) Å and an Au···Au···Au angle of 165.079(12)°.<sup>33</sup> These chains, which involve neutral molecules, both have Au···Au separations that are longer than those in either the colorless or the yellow polymorphs of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>). In the salt (C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>)[Au<sub>2</sub>]<sub>2</sub>, the [Au<sub>2</sub>]<sup>–</sup> ions self-associate into extended chains along a crystallographic 4<sub>2</sub> screw axis with an Au···Au distance of 3.3767(3) Å.<sup>34</sup> As noted above [Au{C(NHCH<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>(PF<sub>6</sub>) also forms linear columns along a crystallographic screw axis with a separation of (3.1882(1) Å).<sup>19</sup> In [(3-picoline)<sub>2</sub>Au][AuCl<sub>2</sub>], where cations and anions associate into zigzagged chains, the Au···Au

separation is somewhat shorter, 3.1538(12) Å.<sup>31</sup> Only in [(tetrahydrothiophene)<sub>2</sub>Au][AuI<sub>2</sub>] are the Au···Au distances (2.967(2) and 2.980(2) Å)<sup>35</sup> as short as those found in the yellow polymorph of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>).

The variation in Au···Au interactions within these polymorphs and within the general class of cations, [(isocyanide)<sub>2</sub>Au<sup>I</sup>]<sup>+</sup>, is remarkable and reflects the generally weak nature of the aurophilic attraction. A different but related form of aggregation is seen in the crystalline forms of {Au(S<sub>2</sub>CN(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>)<sub>2</sub>}.<sup>16</sup> This dimer crystallizes as an orange, luminescent form from dimethyl sulfoxide. In this form, which is a solvate containing dimethyl sulfoxide, the dimers (with an intramolecular Au···Au distance of 2.7690(7) Å) associate through further intermolecular Au···Au contacts with a separation of 2.9617(7) Å into extended chains. In contrast, when crystallized from *n*-propanol/benzene {Au(S<sub>2</sub>CN(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>)<sub>2</sub>} forms colorless, solvent-free crystals in which the shortest intermolecular Au···Au contact is over 8 Å long.

Somewhat related phenomena occur in crystalline salts of the anion [Pt(CN)<sub>4</sub>]<sup>2–</sup> which self-associates to form extended columns with Pt···Pt interactions. In numerous salts of this anion in which different cations and varying amounts of water are present, the Pt···Pt separations cover the wide range from 3.09 to 3.71 Å.<sup>36</sup> However, we are unaware of any examples of polymorphism in [Pt(CN)<sub>4</sub>]<sup>2–</sup> salts. Polymorphism does occur in platinum(II) polypyridine complexes where metal–metal interactions and  $\pi$ – $\pi$  stacking of the aromatic ligands influence the absorption and luminescence of the complexes. For example, (2,2′-bipyridine)Pt<sup>II</sup>Cl<sub>2</sub> crystallizes in a yellow, monomeric form<sup>37</sup> and a red form which contains linear chains of platinum ions with a spacing of 3.402(1) Å.<sup>38</sup> Additionally, [(2,2′,6′,2′-terpyridine)Pt<sup>II</sup>(C≡C–C≡CH)](O<sub>3</sub>SCF<sub>3</sub>) forms a dark-green polymorph with an extended chain structure with a Pt···Pt separation of 3.388 Å and a red form which consists of a chain of dimers with an intradimer Pt···Pt separation of 3.394 Å and an interdimer Pt···Pt separation of 3.648 Å.<sup>39</sup>

The luminescence obtained from [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>), whether in the solid state, in the melt, or in frozen solutions, results from the formation of aggregated species that self-associate through aurophilic attractions. In solution, where the ions are dispersed, [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) is nonluminescent. Additionally, crystalline [(CH<sub>3</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>) (which has no aurophilic interactions) and its solutions are nonluminescent. However, both crystalline forms of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>), which do show strong aurophilic interactions, are luminescent. Moreover, as was the case with the [Au{C(NHMe)<sub>2</sub>}]<sub>2</sub><sup>+</sup> ion, the luminescence is dependent upon the structure of the solid state and the nature of the aurophilic interactions present therein. Within the chains of gold atoms which are present in the polymorphs of [(C<sub>6</sub>H<sub>11</sub>NC)<sub>2</sub>Au<sup>I</sup>](PF<sub>6</sub>), overlap of the occupied gold 5d<sub>z<sup>2</sup></sub> orbitals (where *z* is the axis along the Au···Au···Au chain) produces a filled band of orbitals, while overlap of the empty gold 6p<sub>z</sub> orbitals produces a corresponding band of

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unoccupied orbitals. Excitation of an electron from the filled  $5d_z^2$  band to the empty  $6p_z$  band strengthens the bonding along these chains by removing what is effectively an antibonding electron from the  $5d_z^2$  band and transferring that electron to the bonding  $6p_z$  band. Emission results from the reverse process, transfer of an excited electron from the  $6p_z$  band back to the  $5d_z^2$  band. Similar considerations have been made for related gold isocyanide complexes.<sup>40,41</sup> Additionally, there may be some mixing of the gold  $6p_z$  orbitals with the isocyanide  $\pi$  orbitals, since this mixing is symmetry allowed.

The variations in the luminescence obtained from frozen solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  are likely the result of the formation of a variety of structurally different aggregates that form upon freezing of the solvent. The variations seen in the spectra of solutions with different concentrations of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  indicate that high concentrations of the salt favor the observation of luminescence and that the solutions eventually can become nonluminescent if they are diluted enough. During the freezing process, the concentration of the solute in the unfrozen solvent increases as the solvent itself crystallizes.<sup>42</sup> Under these conditions aggregation of the solute is favored by freezing. The emission bands in the 430–480 nm range in Figures 7 and 8 can be assigned to the formation of extended chain structures which may differ from solvent to solvent in the Au...Au separations, Au...Au...Au angles, and/or the relative orientations of the isocyanide ligands. The emission at shorter wavelength (ca. 380 nm) may be due to dimeric species, since we have observed that dimeric forms of  $[Au\{C(NHMe)_2\}_2]^+$  emit at shorter wavelengths than do salts that consist of extended chains of these cations.<sup>19,20</sup> With the emission seen from the frozen methanol solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ , the band at 482 nm may originate in a columnar structure very similar to that of the yellow polymorph. This frozen solution actually acquires a yellow color upon freezing and the excitation profile for such a frozen solution is similar to that of the yellow polymorph. The emission band seen at 535 nm in the frozen methanol solution may arise from aggregates of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  with even shorter separations than those found in the two polymorphs reported here. These aggregates may include trimers, tetramers, pentamers, etc., as well as interacting chains in which the individual gold centers may have three close Au...Au contacts. Further work on the properties of solutions of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  and related gold(I) complexes are in progress.

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## Experimental Section

**Preparation of the Polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ .** Crystals of the yellow and colorless polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$  were obtained by the procedures reported previously.<sup>22</sup> A 2 equiv amount of cyclohexyl isocyanide was added to an aqueous solution of hydrogen tetrachloroaurate(III) hydrate. After stirring and subsequent filtration, a saturated aqueous solution of ammonium hexafluorophosphate was added. A colorless oil and solid formed immediately. However, upon standing in the aqueous solution, this colorless solid was transformed into a bright yellow, crystalline solid. This easily reproducible process begins when small droplets of oil form on the side of the flask as well as on the surface of the aqueous solution. The formation of this oil was followed by the formation of patches of the yellow solid. This process takes approximately 10 min to complete. Crystals of the yellow polymorph were taken directly from the reaction mixture. Crystals of the colorless polymorph were obtained through dissolving the yellow polymorph in hot 1-propanol followed by cooling.

**X-ray Crystallography and Data Collection.** The crystals were removed from the glass tubes in which they were grown 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 silicone grease and placed in the cold stream of a Bruker SMART CCD with graphite monochromated Mo  $K\alpha$  radiation at 90(2) K. Check reflections were stable throughout 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 the software of SHELXTL 5.1. A semiempirical method utilizing equivalents was employed to correct for absorption.<sup>43</sup> Hydrogen atoms were added geometrically and refined with a riding model.

**Physical Measurements.** Electronic absorption spectra were recorded using a Hewlett-Packard 8450A diode array spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrophotometer.

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**Supporting Information Available:** X-ray crystallographic files for the colorless and yellow polymorphs of  $[(C_6H_{11}NC)_2Au^I](PF_6)$ , and for  $[(CH_3NC)_2Au^I](PF_6)$  (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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