

Formation of a Novel Luminescent Form of Gold(I) Phenylthiolate via Self-Assembly and Decomposition of Isonitrilegold(I) Phenylthiolate Complexes

Robert E. Bachman,^{*,†} Sheri A. Bodolosky-Bettis,[†]
Shana C. Glennon,[†] and Scott A. Sirchio[‡]

Department of Chemistry, Georgetown University
Box 571227, Washington, D.C. 20057-1227
Department of Chemistry and Biochemistry
University of Maryland, College Park, Maryland 20742

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The tendency of gold(I) centers to form relatively strong noncovalent interactions with each other has been well established over the past two decades.¹ These "aurophilic" interactions have been shown to play a critical role in determining both molecular and supramolecular structure in gold-containing compounds.² They have also been suggested to produce and/or modify the luminescent behavior observed for many gold-containing compounds, particularly the gold(I) thiolates.^{2d,3}

Gold(I) thiolates have attracted significant attention over the past half-century because of their importance in the pharmacology of gold.^{1c,4} More recently, the unique properties of the gold-sulfur bond have been extensively exploited for the development of thin-film technologies.⁵ At the molecular level, it has been suggested that the presence of thiolate ligands should strengthen the interactions between gold centers relative to those seen for systems with other anionic ligands, such as the halides.⁶ As part of our investigation into the use of aurophilic interactions for the assembly of well-defined supramolecular architectures, we decided to examine the behavior of systems with the general formula RNCAuSPh (R = *n*-alkyl). To our surprise, these compounds were unstable with respect to the loss of the isonitrile ligand and decomposed to produce a novel, intensely luminescent modification of the polymeric species [PhSAu]_{*n*}. Interestingly, this new modification of gold(I) phenylthiolate appears to form exclusively via the self-assembly and decomposition of the isonitrilegold(I) phenylthiolate complexes that were our intended target.

Addition of PhSNa to methanolic solutions of EtNCAuCl results in the almost instantaneous formation of a white microcrystalline precipitate that is completely insoluble in all common solvents. While the insoluble nature of this material makes it

complete structural characterization difficult, elemental analysis data agree with an empirical formula of [C₆H₅SAu]_{*n*} (**1**).⁷ Irradiation of **1** with UV light (TLC lamp, λ_{ex} = 254/366 nm) results in the emission of an orange-red light that is easily visible to the naked eye in an undarkened room. Measurement of the solid-state fluorescence spectrum (Figure 1) of **1** revealed two emission bands at 465 and 643 nm, with the longer wavelength emission being considerably more intense. The excitation spectrum consists of a broad featureless band centered at approximately 355 nm. Preliminary lifetime data for both emission bands were fit with single-exponential decay curves to yield lifetimes of 5.0 ns (465 nm) and 1.1 μs (643 nm), respectively. The relatively long lifetime of the 643 nm emission is consistent with its assignment to a triplet metal-centered state, while the behavior of the 465 nm band indicates that it arises from a ligand-to-metal charge-transfer-derived state.³

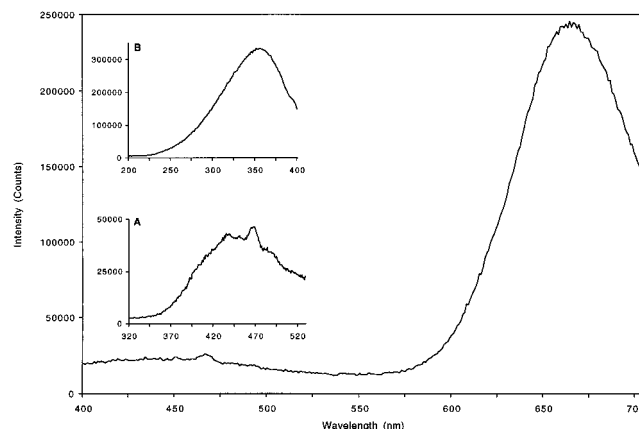


Figure 1. Emission spectrum for **1** with λ_{ex} = 360 nm. Inset A: Magnification of the emission spectrum in the region around 450 nm (λ_{ex} = 275 nm for this spectrum). Inset B: excitation spectrum for **1** with λ_{em} = 660 nm.

The formation of **1** was surprising to us in light of the relative stability of the C–Au bond in isonitrile gold(I) complexes^{1c} and a recent report detailing the structures of two isonitrilegold(I) thiolate complexes.^{2c} Consequently, we were interested in determining how **1** is formed in the above process. Replacing the isonitrile ligand of EtNCAuCl with a longer alkyl chain homolog suppresses but does not halt the formation of **1**. Upon mixing of C₃H₁₁NCAuCl with PhSNa in methanol, there is a several minute induction period before the formation of **1** is first observed, and after 30 min the formation of **1** is still incomplete. Separation of the solution from **1** followed by rapid evaporation of the solvent yielded a small quantity of C₃H₁₁NCAuSPh (**2a**)^{8a} as colorless crystals, along with additional amounts of **1**. The luminescence behavior of **1** produced from this reaction is identical to that produced from EtNCAuCl. By further increasing the length of the alkyl chain of the isonitrile ligand, the formation of **1** may be completely halted during the initial reaction. Mixing C₇H₁₅NCAuCl with methanolic solutions of phenylthiolate produced

(7) Spectral and analytical data for **1**: IR (KBr, cm⁻¹) 3065, 1586, 1484, 1450, 1032, 739, 720. Anal. Calcd for [C₆H₅SAu]_{*n*}: C, 23.54; H, 1.65; Au, 64.34. Found: C, 23.67; H, 1.57; Au, 64.14.

(8) (a) Spectral data for **2a**: IR (KBr, cm⁻¹) 3058, 2954, 2930, 2870, 2248, 1580, 1476, 1089, 1030, 741, 720; ¹H NMR (CDCl₃, ppm) 7.53 (2H, d, *J* = 8.1 Hz), 7.10 (2H, t, *J* = 7.8 Hz), 6.99 (1H, t, *J* = 7.8 Hz), 3.61 (2H, tt, *J*_{H–H} = 7.9 Hz, *J*_{N–H} = 1.2 Hz), 1.83 (2H, m), 1.42 (4H, m) 0.95 (3H, t, *J* = 7.2 Hz). (b) Spectral data for **2b**: IR (KBr, cm⁻¹) 3051, 2592, 2932, 2868, 2253, 1584, 1471, 1085, 1030, 736, 715; ¹H NMR (CDCl₃, ppm) 7.52 (2H, d, *J* = 8.1 Hz), 7.10 (2H, t, *J* = 7.9 Hz), 6.99 (1H, t, *J* = 7.9 Hz), 3.60 (2H, t, *J*_{H–H} = 7.2 Hz), 1.83 (2H, m), 1.42 (2H, m), 1.32 (6H, m), 0.95 (3H, t, *J* = 6.9 Hz).

[†] Georgetown University.
[‡] University of Maryland.

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no noticeable precipitate after 30 min, and evaporation of the solvent yielded the isonitrile gold(I) thiolate complex, $C_7H_{15}NCAuSPh$ (**2b**), as the only product in good yield.^{8b} However, crystalline samples of **2b** left to stand for several days become progressively more insoluble and begin to display luminescence behavior identical to that of samples of **1** prepared in solution from either $EtNCAuCl$ or $C_5H_{11}NCAuCl$. This process can be accelerated considerably by gently heating **2** in vacuo; however, samples of **1** produced in this manner have a slight gold tint, indicating that a small amount of decomposition occurred as well.

The isolation of the isonitrile complexes **2a** and **2b**, as well as the solid-state conversion of **2b** to **1**, provides convincing evidence that the initial product formed in all of the above reactions is the isonitrilegold(I) thiolate complex. Furthermore, the rate at which **1** forms is directly correlated with the chain length, and by extension the volatility, of the isonitrile ligand. An additional interesting aspect of these results is that the luminescent behavior of **1** appears to depend on its formation via decomposition of the isonitrile complexes. Preparation of samples of $[PhSAu]_n$ via the previously reported procedures,⁹ such as the reaction of Me_2SAuCl with $PhSNa$ or the reaction of $PhSH$ with $HAuCl_4$, produces materials with the correct elemental composition but that show no luminescence and are amorphous (as judged by XRD). However, this amorphous material may be transformed into **1** by reaction with a catalytic amount (~ 5 mol %) of an isonitrile in hot MeOH. Interestingly, DSC measurements show a difference in the thermal behaviors of **1** and amorphous $[PhSAu]_n$. The amorphous material displays a strong exothermic process, which is absent for **1**, just before the onset of decomposition at 255 °C. The origin of this extra peak is currently unclear, as visual observation shows only the same decomposition observed for **1** occurring.

To better understand the role that the isonitrile ligands play in the formation of **1**, we undertook structural studies of **2a** and **2b**.¹⁰ At the molecular level, these two complexes differ only in the length of the alkyl chain and all bonding parameters agree with expectations. At the supramolecular level, both **2a** and **2b** aggregate in an antiparallel fashion into dimeric units via Au–S (**2a**, $3.663(2)$ Å; **2b**, $3.6858(15)$ Å) and weak aurophilic interactions (**2a**, $3.7858(6)$ Å; **2b**, $3.6105(5)$ Å). The dimer units in turn come together in a parallel manner via additional weak Au–S interactions (**2a**, $4.060(2)$ Å; **2b**, $4.0224(16)$ Å), resulting in a motif that can be described as a “crinkled tape” (Figure 2). The tapes

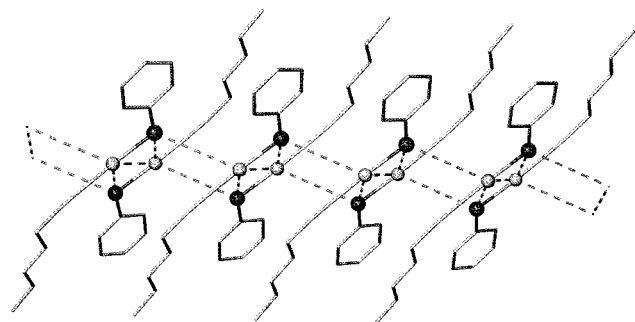
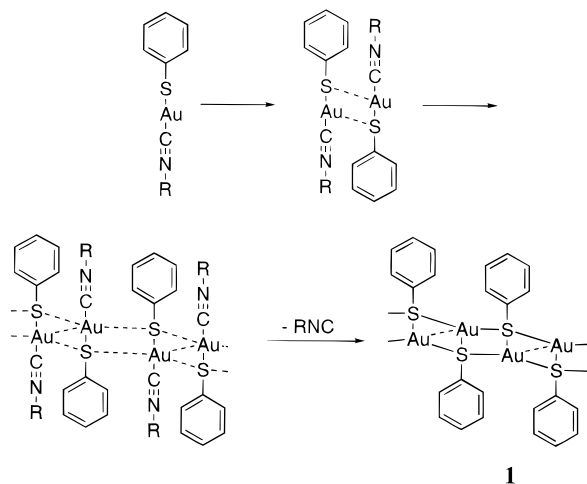


Figure 2. Packing diagram for **2a** showing the “crinkled tape” motif formed by the Au–S and Au–Au interactions. The dotted lines indicate the Au–S and Au–Au interactions.

stack together in an antiparallel fashion via van der Waals contacts between alkyl chains and phenyl rings on adjacent tapes.

This supramolecular motif, combined with the observed solid-state transformation of **2b**, suggests a structure for **1** such as that shown in Scheme 1. Preliminary attempts to index the powder XRD pattern of **1** have yielded a unit cell consistent with the proposed structure. Additionally, the structural results combined with the catalytic ability of the isonitriles to produce **1** allude to a possible mechanism for its formation involving the complementary self-recognition and self-assembly of the isonitrile complexes, either in solution or as crystallization occurs, followed by loss of the isonitrile ligand. We are currently working to confirm the structure of **1** as well as the proposed mechanism for its formation. Studies are also underway that explore how the identity of the thiolate influences the physical properties of related gold(I) thiolate polymers.

Scheme 1. Proposed “Mechanism” for the Self-Recognition and Assembly of $RNCAuSPh$ Molecules and the Subsequent Formation of **1** from the Resulting Supramolecular Polymer



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Supporting Information Available: Displacement ellipsoid plots, tables of crystal data, structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic parameters for **2a** and **2b** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(10) Crystallographic data for **2a**: $C_{12}H_{16}AuNS$, FW 403.28, triclinic space group $P1$ (No. 2), $a = 5.5295(4)$ Å, $b = 7.6073(5)$ Å, $c = 16.6967(12)$ Å, $\alpha = 89.0530(10)^\circ$, $\beta = 80.5330(10)^\circ$, $\gamma = 69.0710(10)^\circ$, $V = 646.39(8)$ Å³, $Z = 2$, Bruker SMART CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $T = -50$ °C, 7402 reflections measured, 3095 unique ($R_{int} = 0.0393$), $wR2 = 0.1055$ (all data), $R1 = 0.0433$ (2466 data with $I > 2\sigma(I)$), GOF = 1.035. Crystallographic data for **2b**: $C_{14}H_{20}AuNS$, FW 431.34, triclinic space group $P1$ (No. 2), $a = 5.4405(4)$ Å, $b = 7.5603(5)$ Å, $c = 18.7189(12)$ Å, $\alpha = 87.6570(10)^\circ$, $\beta = 87.1010(10)^\circ$, $\gamma = 70.4210(10)^\circ$, $V = 724.26(9)$ Å³, $Z = 2$, Siemens SMART CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å), $T = -100$ °C, 8259 reflections measured, 3440 unique ($R_{int} = 0.0417$), $wR2 = 0.0686$ (all data), $R1 = 0.0324$ (2715 data with $I > 2\sigma(I)$), GOF = 0.865.