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Modulation of Luminescence by Subtle Anion−Cation and Anion−π Interactions in a Trigonal Au$^{I}\cdots$Cu^{I} Complex

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Supporting Information

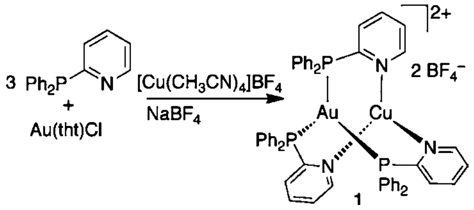
ABSTRACT: The trigonally coordinated [AuCu(PPh$_2$py)$_3$](BF$_4$)$_2$ (**1**) crystallizes in two polymorphs and a pseudopolymorph, each of which contains a trigonally coordinated cation with short Au^{I}−Cu^{I} separations of ~2.7 Å. Under UV illumination, these crystals luminesce different colors ranging from blue to yellow. The structures of these cations are nearly superimposable, and the primary difference resides in the relative placement of the anions and solvate molecules. As confirmed by time-dependent density functional theory calculations, it is these interactions that are responsible for the differential emission properties.

Heterometallic interactions with Au^{I} produce interesting structural and optical properties.[1] While there are numerous reports of two-coordinate Au interacting with a heterometallic atom,[2] the corresponding metal−metal associations in three-coordinate Au^{I} systems are quite rare. This is surprising given that coordination of a third ligand to a Au^{I} center would increase the dispersivity and, hence, enhance any subsequent metallophilic interaction. Nonetheless, a search of the CCDC yields relatively few structures with AuP$_3$−M interactions. Of these, only 11 are heterometallic systems, and most are cage complexes where the heterometal is incarcerated inside of a gold−metallocryptand cage.[3] No trigonally coordinated AuP$_3$ interactions to Cu^{I} were found. Recently, we reported a vapochromic Au^{I}−Cu^{I} complex employing a pyridyl-substituted N-heterocyclic carbene ligand where solvent ligation modulates the Au^{I}−Cu^{I} interaction and the photoemission.[4] This prompted us to question whether similar properties would be present in simple phosphinopyridyl-bridged gold−copper systems. Much to our surprise, we discovered a previously unknown structural arrangement, two polymorphs, a pseudopolymorph, and their dramatic changes in emission as a function of solvent and/or anion coordination.

In 1997, Schmidbaur and co-workers reported the preparation of the bimetallic mixed-metal species [AuCu(PPh$_2$py)$_2$](BF$_4$)$_2$ but were unable to structurally characterize it.[5] However, in our hands (Scheme 1), only the three-coordinate [AuCu(PPh$_2$py)$_3$](BF$_4$)$_2$ (**1**) could be isolated regardless of the metal-to-ligand stoichiometry. More interestingly, this complex crystallizes in at least two polymorphs and a pseudopolymorph that exhibit blue, green, or yellow photoluminescence.

As previously reported, the reaction of Au(tht)Cl (tht = tetrahydrothiophene) with diphenylphosphinopyridine and [Cu(NCCH$_3$)$_4$]BF$_4$ produces a dynamic species whose ^{31}P{^{1}H} NMR spectrum (acetone-d_6) shows a broad peak at 48.6 ppm indicative of Cu^{I} dissociation. Crystallization by the vapor diffusion of diethyl ether into methanol solutions reproducibly yields blue, green, yellow, orange, and red luminescent crystals labeled **1a**−**1e** in Figure 1. X-ray-quality crystals were obtained for **1a**−**1c** and **1e**. The orange form (**1d**) tended to be microcrystalline or a powder, whereas the red-luminescent species (**1e**) was determined to be a multimetallic cluster, [Au$_3$Cu$_2$(PPh$_2$py)$_5$](BF$_4$)$_5$, where each Cu center face-caps the triangular Au$_3$ unit (see the Supporting Information, SI). The cationic portions of **1a**−**1c** are nearly superimposable except that one phenyl ring in **1c** is slightly twisted (see the SI). Each cation contains a three-coordinate Au^{I} center connected to the trigonally coordinated Cu^{I} center by the three spanning phosphinopyridyl ligands with short Au1−Cu1 separations of 2.7179(9), 2.7077(5), and 2.7328(3) Å for **1a**−**1c**, respectively. The blue form (**1a**) is a pseudopolymorph of composition of **1**·3.5CH$_3$OH, while the green and yellow forms are true polymorphs of **1**·2CH$_3$OH. The fundamental difference between these three species resides in the relative orientation

Scheme 1



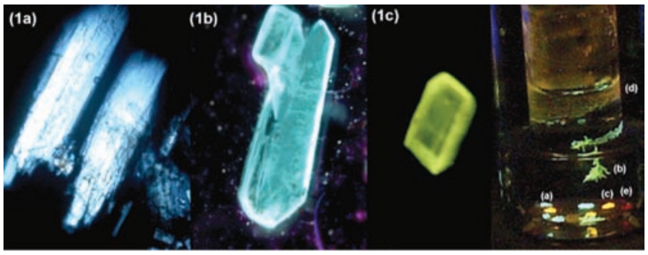


Figure 1. Microscope photographs of individual crystals of **1a**, **1b**, and **1c** and photograph of crystallization vial of all forms (**a-e**) under UV light (λ_{ex} =365 nm). Colors from different cameras are not calibrated.

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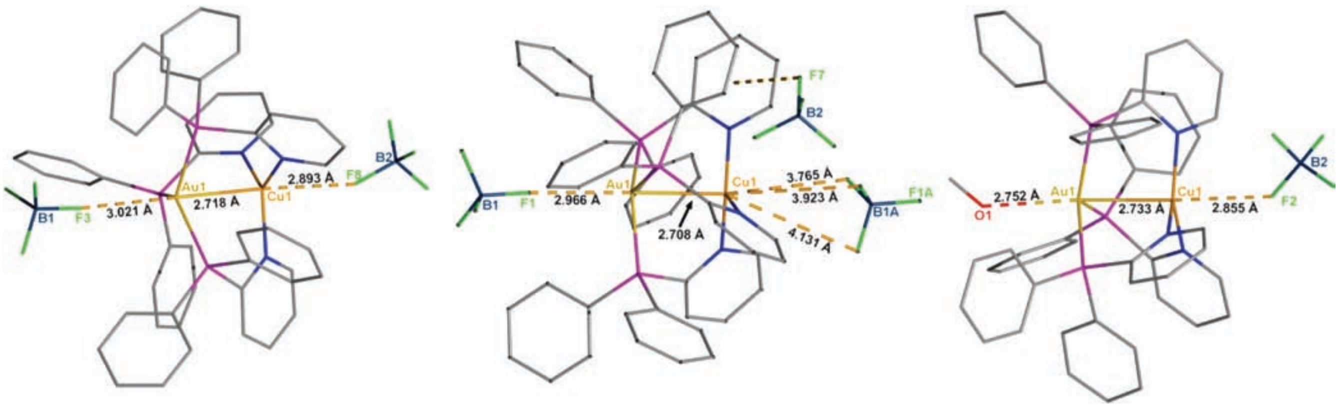

Figure 2. X-ray structures of **1a** (left), **1b** (middle), and **1c** (right). In **1b**, the B1a-labeled anion is a symmetry generation.

of the cations with respect to the BF_4^- anions, the methanol solvates, and the interligand $\pi_{ph}-\pi_{py}$ interactions.

As shown in Figure 2, the cations of **1a**−**1c** associate with the BF_4^- anions and/or a methanol solvate in three unique arrangements. In **1a**, the cation is straddled by two BF_4^- anions, one in a linear coordination mode with a B1−F3−Au1 angle of 174.88°, while the other coordinates to the Cu center in a bent arrangement with a B2−F8−Cu1 angle of 151.14°. Additionally, the three pyridyl rings form π stacks with phenyl rings on the adjacent ligands with short centroid−centroid separations of 3.547, 3.641, and 3.646 Å. In the green-emitting complex, **1b**, the Au^I center similarly interacts with a BF_4^- anion (B1−F1−Au1 = 175.5°); however, these interactions on the Cu center are lost, and only much longer separations (>3.7 Å) to a symmetry-equivalent BF_4^- anion in a neighboring asymmetric unit are observed. Additionally, compared to **1a**, slightly longer aryl−aryl interactions of 3.751, 3.769, and 3.811 Å are measured in **1b**. Interestingly, the pyridyl ring of the shortest pair is in close contact with the F atom of a BF_4^- anion with a $F-py_{centroid}$ separation of 3.547 Å. The F atom is positioned closer (<3.4 Å) to the C atoms of the C37−C38 ring juncture and ~4.2 Å from the N atom of the pyridyl ring. In the yellow-emitting **1c**, a methanol solvate replaces the anion binding at the Au^I center, while a BF_4^- anion weakly coordinates to the Cu^I center in a bent orientation (B2−F2−Cu1 = 130.77°). There are two short pyridyl−phenyl interactions of 3.557 and 3.632 Å and one long interaction at 3.915 Å. The association of solvent or weakly coordinating anions like BF_4^- is not unusual.[6] In fact, Wang and co-workers[7] recently reported the related homometallic complex $[Cu_2(PPh_2py)_3](BF_4)_2$, which contains both an auxiliary solvent coordinated to one Cu center and a $Cu-FBF_3$ interaction along with important $\pi-\pi$ interactions.

In solution, these interactions are lost, and the complex dissociates Cu^I ion, producing nonluminescent solutions. However, crystals of **1a**−**1c** and the unidentified material **1d** are highly photoluminescent. Emission and excitation spectra (see the SI) were collected by selectively probing different portions of the crystallization vial to avoid desolvation upon exposure to air. The green- and yellow-emitting crystals are fairly stable to the atmosphere and do not readily desolvate; however, the blue crystals quickly lose solvent to form orange-emitting powders. Once desolvated, these powders can be reconverted into their solvated forms by recrystallization. Exposure to solvent vapor does not reconstitute the original solids. Excitation of a crystalline sample of **1a** at 365 nm produces a broad emission band at 493 nm. For **1b**, this band red-shifts to 530 nm, and finally in **1c**, this band is observed at 550 nm.

It is tempting to assign the progressive red shifting observed in **1a**−**1c** to a simple perturbation of the metal centers by solvent and anion coordination; however, given the structural similarity of the cations, it is likely that a more complex mechanism is at play. All three cations have similar Au−Cu separations (within 0.025 Å), and the emission maxima do not trend with these distances. More likely, the emission is influenced by subtle differences in anion−cation, $\pi-\pi$, and anion−π interactions. There is literature precedence for such an assignment, though many other possibilities have been reported in related $d^{10}-d^{10}$ systems. For example, in the simple trigonal AuP_3 complexes, the emission is thought to arise from a metal-centered $d_{xy},d_{x^2-y^2}$ to p_z transition[8] or one with significant contributions from the ligand orbitals.[9] In the absence of exciplex formation,[10] the emission in the related phosphine-bridged bimetallic complexes, $[Au_2(dmpm)_3]^{2+}$, was assigned to a mononuclear d-to-p transition that is perturbed by the second Au center.[11] However, calculations[7] on the closely related $[Cu_2(PPh_2py)_3]^{2+}$ system suggest significant ligand character in both the ground and excited states and further that ligand $\pi-\pi$ interactions "profoundly influence the emission energy". Likewise, the importance of intraligand $\pi-\pi$ interactions is echoed in the luminescent properties of tetrahedral $[Au(dppb)_2]^+$ complexes, whose emission varies from blue to orange depending on the ligand orientation.[12] Meanwhile, in the mixed-metal Au^I-Cu^I phosphinopyridyl-bridged clusters, a metal-to-ligand charge-transfer (MLCT) state mixed with an intraligand CT state was proposed.[13] Similarly, a MLCT state that could be tuned by substitution was implicated in a series of perhalophenyl Au−Cu pyrimidine complexes.[14] Finally, ligand-to-metal CT states from the π-basic Spy ligand are suspected in the loosely related $[AuCu(Spy)(PPh_2py)]^+$ system.[15]

To understand the origins of the differential emission of **1a**−**1c**, electronic structure calculations were undertaken (see the SI). For all three complexes, the first series of singlet−triplet excited states are best described as ligand-based pyridyl−π^* in nature (Figure 3). Complexes **1a** and **1c** also have similar ground-state wave functions that are mostly $Cu(3d_{x^2-y^2})$ in nature. The significant red shift in the emission wavelength (calcd λ_{em} = 414.78 nm for **1a** and λ_{em} = 557.26 nm for **1c**) comes from two effects. The first effect originates from greater π stacking between the pyridyl and phenyl rings in **1c** versus **1a**, as revealed in a quantum theory of atoms in molecules (QTAIM) analysis (see the SI). There are more bond paths

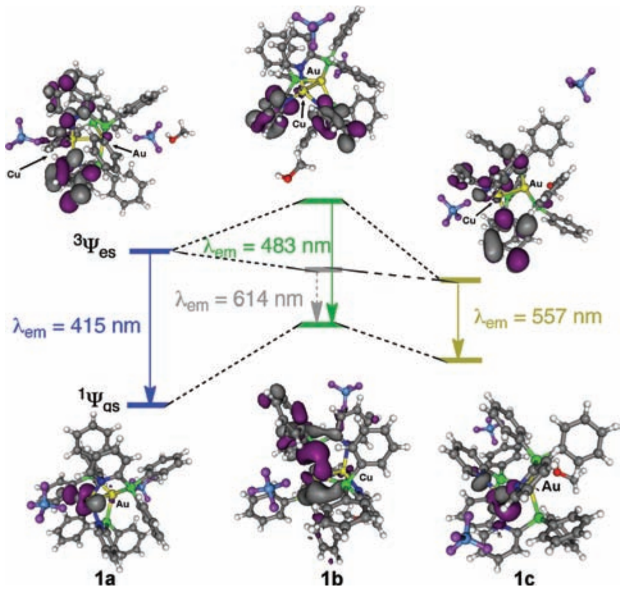

Figure 3. Time-dependent density functional theory calculations (B(HF38)P86/def2-TZVPP/def2-TZVP-ECP) on **1a**−**1c** showing isosurface plots of ground- and excited-state wave functions for the lowest-energy triplet−singlet emission. For compound **1b**, the higher-energy emission is for the compound that has the BF_4^- anion associated with the py/ph π system, and the lower-energy emission has the BF_4^- anion removed from the py/ph π system.

between the pyridyl and phenyl rings of **1c** than **1a**, which results in stabilization of the pyridyl-based excited state in **1c** relative to **1a**. The other effect is destabilization in the Cu-based ground state of **1c** versus **1a**. In all three complexes, there is some Au−Cu bonding. Coordination of the methanol in place of the BF_4^- anion (QTAIM analysis; SI) leads to a more electron-rich Au^I center, which, in turn, destabilizes the Cu-based HOMO. These two effects act in concert to significantly red shift the emission in **1c** versus **1a**.

The nature of the ground state in **1b** is significantly different from that in both **1a** and **1c**. Unlike in **1a** and **1c**, the BF_4^- anion is no longer coordinated to the Cu^I center, as suggested by QTAIM analysis. This stabilizes the Cu-based frontier orbitals relative to the Au-based ones, and the ground state is now predominantly $Au(5d_{x^2-y^2} + 5d_{z^2})$ in nature. Furthermore, there is significantly more metal−metal character in the HOMO of **1b** than in **1a** and **1c**. Thus, the ground-state wave function is higher in energy in **1b** than in either **1a** or **1c**. This is coupled with association of a BF_4^- anion with the pyridyl−phenyl π system, which raises the excited-state energy through both electrostatic effects and disruption of π stacking. These two effects result in a singlet−triplet emission energy that is intermediate of **1a** and **1c** (calcd λ_{em} = 482.96 nm). Computationally, we probed the supposition of the anion and its effect on the excited-state destabilization. Relocating the BF_4^- anion from the π system to periphery of the Cu center (the B1a anion in Figure 2) significantly stabilizes the excited state and red-shifts the emission for **1b** to 614.44 nm. Along these lines, one could speculate that the orange form, **1d** above, would have a structure similar to that of **1b** except without the destabilizing BF_4^-−π interaction.

These results illustrate the importance of subtle noncovalent interactions on the energies of both the ground and excited states. It is remarkable that simple crystallization of **1** yields multiple crystals with seemingly similar structures, yet quite varied solid-state photophysical properties. The lack of significant Au participation in the emission of **1a** and **1c** was also unexpected and underscores the importance of "the other metal" in the study of Au^I mixed-metal interactions. Given the facility in which an anion or solvent molecule can influence the electronics, it is reasonable that other systems would possess similar interactions and that the resulting solid-state emission could be modulated by simple and judicious anion or solvent substitution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization, and single-crystal X-ray diffraction data including thermal ellipsoid plots, overlay of cations, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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