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Unsupported Gold(I)–Copper(I) Interactions through η^1_{Au}-$[Au(C_6F_5)_2]^-$ Coordination to Cu^+ Lewis Acid Sites

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The reaction of the complex $[Au_2Ag_2(C_6F_5)_4(N{\equiv}CCH_3)_2]_n$ (**1**) with 1 equiv of CuCl in the presence of 1 equiv of pyrimidine ligand leads to the formation of the heteronuclear Au(I)–Cu(I) organometallic polymer $[Cu\{Au(C_6F_5)_2\}(N{\equiv}CCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$ (**2**) through a transmetalation reaction. Complex **2** displays unprecedented unsupported Au(I)···Cu(I) interactions of $[Au(C_6F_5)_2]^-$ units with the acid Cu(I) sites in a $[Cu(N{\equiv}CCH_3)(\mu_2\text{-pyrimidine})]^{n+}{}_n$ polymeric chain. Complex **2** has a rich photophysics in solution and in the solid state.

Metallophilic interactions between gold(I) and closed-shell metal atoms (Au···M) have attracted great interest over the past years due to their theoretical interest,[1] the photophysical properties of the complexes,[2] and their potential applications.[3] Unsupported Au···M interactions not imposed by molecular architecture, such as bridging ligands or hydrogen bonding, are of particular interest.[4]

Nevertheless, the number of different metallic centers that give weak and unsupported interactions with gold is very limited. Members of the same group or near to it are electronically the most favorable candidates for such Au···M interactions. For example, compounds with Au(I)−Ag(I) interactions are well documented although they are not a very broad class.[5] However, as far as we are aware, there is no evidence of complexes with unsupported Au(I)−Cu(I) interactions. Although cuprophilicity (i.e., Cu(I)−Cu(I) bonding interaction) has been questioned,[6] Che and coworkers have recently reported spectroscopic and structural evidence for these Cu(I)···Cu(I) interactions in dinuclear Cu(I) diphosphane complexes.[7] The preparation of such bimetallic complexes opens a new field of study since, in addition to the intrinsic features of Au(I),[8] Cu(I) can provide useful photophysical properties such as long emission lifetimes (i.e., $\tau > 1\ \mu s$). In addition, Cu(I) has a high affinity for N-donor ligands that are constituents of biological substrates,[9] and for example, photoactive copper(I) complexes have been reported to act as spectroscopic reporter probes for relaying information about DNA conformation.[10]

We have succeeded in synthesizing gold(I) complexes with heterometals, such as Ag(I) or Tl(I), using the Lewis acid−base strategy.[3,4,11] Nevertheless, reactions between $[AuR_2]^-$ (R = perhalophenyl) anions and Cu(I) inorganic salts do not give satisfactory results in the synthesis of Au(I)−Cu(I) materials. An alternative synthetic route for such compounds

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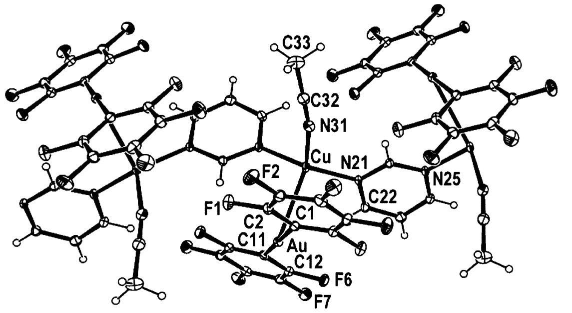
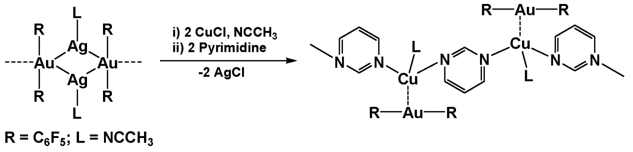


Figure 1. Crystal structure of **2**. Selected bond lengths [Å]: Au−Cu 2.8216(6), Au−C(1) 2.056(5), Au−C(11) 2.045(5), Cu−N(21) 1.987(3), Cu−N(25)#1 2.003(4), Cu−N(31) 2.048(4). #1: *x*, −*y* + 1/2, *z* − 1/2.

Scheme 1. Synthesis of $[Cu\{Au(C_6F_5)_2\}(N{\equiv}CCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$ (**2**)



is the use of a more easily accessible Au(I)−Ag(I) complex as a precursor for a transmetalation reaction with a Cu(I) salt.

Here we report the synthesis, crystal structure, and luminescence properties of the complex $[Cu\{Au(C_6F_5)_2\}(N{\equiv}CCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$ (**2**) ($C_4H_4N_2$ = pyrimidine), in which Au(I)···Cu(I) unsupported interactions are observed for the first time in the solid state. The photoluminescent properties of this complex are also described.

By taking advantage of the propensity of Cu(I) to form stable derivatives in the presence of acetonitrile, treatment of $[Au_2Ag_2(C_6F_5)_4(N{\equiv}CCH_3)_2]_n$ (**1**) (see Supporting Information) with CuCl and pyrimidine yields complex $[Cu\{Au(C_6F_5)_2\}(N{\equiv}CCH_3)(\mu_2\text{-}C_4H_4N_2)]_n$ (**2**) (see Scheme 1).

The crystal structure of **2** (Figure 1)[12] consists of a polymeric chain that runs parallel to the crystallographic *z* axis and is formed by the repetition of dinuclear units joined together by bridging pyrimidine ligands that bind two Cu(I) ions (Cu−N: 1.987(3), 2.003(4) Å). The Cu(I) centers display a distorted tetrahedral environment by the additional coordination to an acetonitrile molecule (Cu−N: 2.048(4) Å) and the gold atom of a linear $[Au(C_6F_5)_2]^-$ unit via an unsupported Au···Cu bonding interaction of 2.8216(6) Å. The intramolecular Au···Au separation is longer than 6 Å, so the $[Au(C_6F_5)_2]^-$ fragments are connected to the chain only via unsupported Au···Cu interactions.

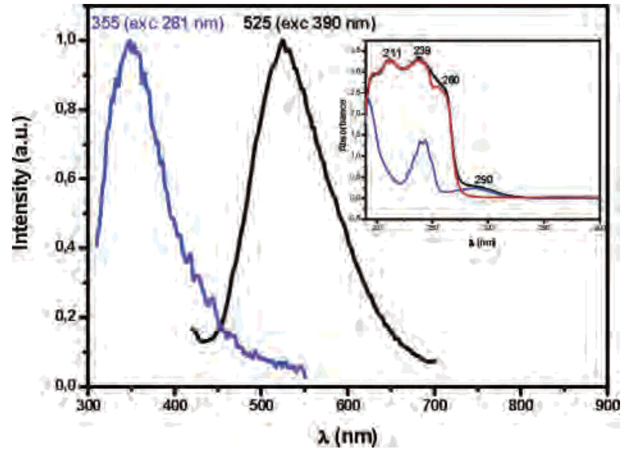


Figure 2. Normalized emission spectra of complex **2** in the solid state (max at 525 nm) and in MeOH solution (max at 355 nm) at room temperature. Inset: UV−vis absorption spectra of complex **2** (black line), the precursor $NBu_4[Au(C_6F_5)_2]$ (red line), and pyrimidine ligand (blue line) in acetonitrile solution ($5{\cdot}10^{-4}$ mol·L^{-1}).

Complex **2** shows very interesting photophysical properties. It is strongly luminescent at room temperature (Figure 2) and at 77 K in solid state, displaying broad and unstructured emissions at 525 (max ex 390) and 529 nm (max ex 371 nm), respectively, showing an interesting degree of rigidochromic effect.[13] The lifetime in solid state at room temperature fits a monoexponential decay with a value of 10.3 ± 0.2 μs, which suggests a phosphorescent process. The absorption spectrum in degassed acetonitrile (inset in Figure 2) shows peaks at 211 ($\epsilon = 6.6 \times 10^3$ mol^{-1} dm^3 cm^{-1}), 239 ($\epsilon = 6.7 \times 10^3$), 260 ($\epsilon = 5.2 \times 10^3$), and a shoulder at 290 nm ($\epsilon = 0.5 \times 10^3$). The first three peaks appear at similar wavelengths to those in the precursor complexes, and therefore, we assign them tentatively to $\pi\pi^*$ transitions in the pentafluorophenyl rings.[14] In the case of the pyrimidine ligand, the absorption spectrum in the same solvent (inset Figure 2) displays three peaks at 193 ($\epsilon = 4.6 \times 10^3$ mol^{-1} dm^3 cm^{-1}), 240 ($\epsilon = 2.7 \times 10^3$), and 286 nm ($\epsilon = 0.46 \times 10^3$). The coincidence in energy and intensity of the latter with that of complex **2** placed at lower energy prompted us to assign it to a transition in the pyrimidine ligand. Very interestingly, complex **2** is also luminescent in solution showing solvent dependence. It shows an emission band at 355 nm (ex 281 nm) in methanol (Figure 2) or 365 nm (ex 290 nm) in acetonitrile, but two bands at 394 (ex 263) and a less intense band at 530 nm (369 nm) in dichloromethane. The high energy emissions are not likely to be due to gold or copper centered transitions since these should appear at higher wavelengths.[2,7a,9,15] In addition, pyrimidine is also luminescent in solution displaying an emission at 365 nm (ex 270 and 308 nm) in methanol or 369 nm (ex 314 nm) in acetonitrile. The similar energies found for the emissions of complex **2** and pyrimidine in these solvents prompted us to tentatively assign these bands as intraligand transitions. In the case of the weak lower energy emission in dichloromethane, it appears at fairly similar

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(12) Crystal data of complex **2**: $C_{18}H_7AuCuF_{10}N_3$, monoclinic, $P2_1/c$, $a = 8.9212(2)$ Å, $b = 19.5995(4)$ Å, $c = 11.4980(2)$ Å, $\beta = 101.555(1)°$, $V = 1969.69(7)$ Å^3, $Z = 4$, $\mu = 8.624$ mm^{-1}, 32535 reflections $2\theta_{max}$ 58°, 5078 unique ($R_{int} = 0.0580$), $R = 0.0316$, $R_w = 0.0696$ for 299 parameters, 115 restrictions, $S = 1.030$, max $\Delta\rho = 1.981$ e Å^{-3}. Crystal data for **2** were measured at −100 °C using a Nonius KappaCCD diffractometer, Mo Kα radiation, ω- and ϕ-scans. The structure was solved by direct methods and refined anisotropically on F^2 (Sheldrick, G. M. *SHELXL-97*; Univerity of Göttingen: Göttingen, Germany). Absorption correction: multiscan.

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energy as in the solid state, and therefore, we propose a similar origin.

The assignment of the excited state for complex **2** is difficult because there are several possibilities, including metal to ligand charge transfer (MLCT), metal centered (MC), or ligand to ligand charge transfer (LLCT) transitions. An interligand charge transfer is highly unlikely due to the relatively low energy of the observed emission, and for copper(I) complexes bonded to aromatic nitrogen donor ligands, the most common assignment is metal to ligand charge transfer.[10,15−18] The results in solution agree with this last assignment, since the lack of the low energy emission in these basic solvents can be interpreted in terms of an exciplex quenching mechanism where the formally d^9 copper in the MLCT state is susceptible to reaction with nucleophiles. In particular, the development of Cu(II) character in the excited state results in a flattening distortion and allows an associative attack by the solvent, resulting in stabilization of the excited state and destabilization of the ground state, which inevitably promotes quenching.[10,19] In fact, Cu(II) compounds are frequently five-coordinate. Interestingly, the quenching process occurs also at low temperature in glass media (EtOH/MeOH 1:4). By contrast, in the case of dichloromethane, its poor ligand properties prevent the formation of the exciplex, and thus, both bands are present in the spectra.

Finally, emission signals from charge transfer excited states of copper(I) are typically weak and short-lived,[10,20,21] but this complex displays a strong luminescence that we tentatively assign to a LMCT phosphorescent process. We interpret this result in terms of the Lewis basic character of the gold center interacting with the copper(I) Lewis acid, which favors the copper to the pyrimidine ligand charge-transfer transition, although a MC (Cu) transition cannot be excluded.

These preliminary results illustrate the easy access to a new class of heterometallic Au(I)−Cu(I) compounds that, indeed, display very interesting photophysical properties and potential applications that are now under investigation. Future ligand variations as well as theoretical studies will surely provide more information about the nature of the Au(I)···Cu(I) interaction.

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Supporting Information Available: X-ray crystallographic data in CIF format for **2**; experimental procedure, characterization data, and photophysical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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