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Novel Luminescent Au(I) Pyrimidinethiolate Dimer Having an Unusual π-Stacking Structure

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The structures and bonding of Au(I) compounds have generated considerable interest, stimulated in part by real or potential application of these systems as sensitizers for photographic emulsions,[1−3] and luminescence-based chemical sensors.[4−6] Most Au(I) compounds possess linear coordination geometries and show evidence of aurophilic interactions leading to dimeric and/or polynuclear structures.[4,7−12] Closed-shell aurophilic interactions are estimated to be energetically similar to hydrogen bonds (ca. 5−7 kcal/mol), and it has been suggested that they serve as a major determinant of the packing of Au(I) systems in the solid state.[7] Recent communications have described using aurophilic interactions in conjunction with H-bonding or $\pi-\pi$ interactions as a means of generating extended or supramolecular structures.[12−16] In this Communication, we describe two new Au(I) pyrimidinethiolate compounds including a dimer that possesses a solid state structure in which π stacking clearly dominates over intermolecular Au···Au bonding. In fluid solution, the dimer dissociates easily and shows concentration dependent luminescence.

The dimeric Au(I) complex [Au(4,6-Me$_2$pym-2-S)]$_2$, **1**, is prepared by the addition of 1 equiv of 4,6-dimethylpyrimidinethiolate in methanol to a solution of AuCl(SMe$_2$) in CH$_2$Cl$_2$. After recrystallization from hot DMSO, **1** is obtained analytically pure in ca. 40% yield as yellow microcrystalline needles. A single-crystal X-ray structure analysis of **1**·DMSO reveals two independent but essentially identical molecules, each with $\bar{1}$ symmetry, having the arrangement shown in Figure 1.[17] The molecular structure is typical of binuclear gold(I) systems with approximately linear S−Au−N coordination at each metal center and pyrimidinethiolate ligand bridges. The intramolecular Au···Au distances in the two molecules average 2.7365 Å, which is relatively short for those found in dimeric Au(I) complexes.[18−21]

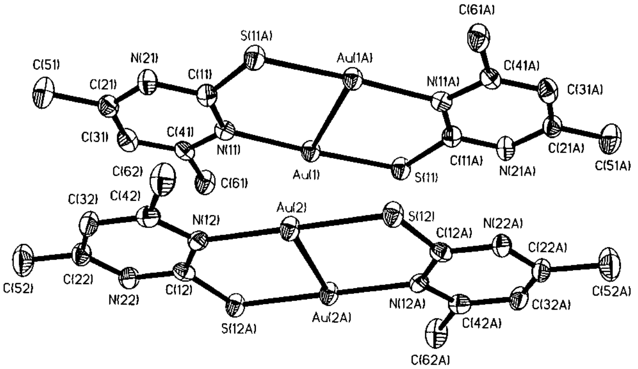

Figure 1. Perspective view of the molecular structure of the dimer **1**.

The most striking feature of the crystal structure is the packing of the planar dimers within the crystal. Instead of the commonly observed arrangement determined by *intermolecular* aurophilic interactions leading to chains of Au(I), the planar dimers stack along the *a* axis with the pyrimidine moieties in adjacent molecules overlapping. The interplanar distances between the overlapping pyrimidine ligands within pairs of dimers are 3.416(1) and 3.474(1) Å, indicative of effective $\pi-\pi$ interactions, while the intermolecular Au···Au separations of 3.544(1) and 3.783(1) Å are relatively long compared with the 3.0−3.2 Å range cited as evidence of aurophilic interaction.[7,18]

The ^{1}H NMR spectrum of **1** in DMF-d$_7$ at room temperature shows broad resonances at δ 7.07, 2.80, and 2.38 ppm, assignable to the single aromatic proton and the two inequivalent methyl group protons of the pyrimidinethiolate ligand. Upon a modest increase in temperature to 30 °C, coalescence of the two methyl resonances is observed, indicating that **1** is stereochemically nonrigid. A variable temperature ^{1}H NMR study carried out between −20 and +70 °C gave activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 21.0 kcal/mol and +23.2 cal/mol·K for the process,[22] consistent with a mechanism involving Au−N bond cleavage (possibly solvent-assisted) and opening of one of the ligand bridges. Complete dissociation of **1** into solvated monomers is also possible.[23]

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(17) Crystal data for **1**·DMSO: monoclinic, space group $P2_1/n$, a = 7.1110(2) Å, b = 16.0299(5) Å, c = 16.6789(5) Å, β = 99.280(1)°, V = 1876.3(1) Å^3, Z = 4, temp = 193(2) K, Siemens SMART diffractometer, Mo Kα radiation (λ = 0.710 73 Å), 3.5° < 2θ < 46.5°, 8150 measd data, 2671 unique, 2358 obsd with $I > 2\sigma(I)$, full-matrix F^2 refinement, R1 = 0.024, wR2 = 0.054 (all data).

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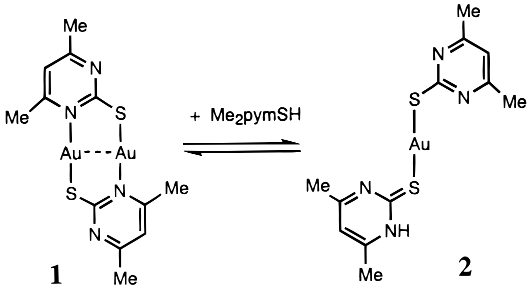
The addition of free 4,6-dimethylpyrimidinethiol to a solution of **1** reveals facile ligand exchange that appears to take place even faster than the fluxional process. With a 1:10 ratio of free ligand: **1**, the ^1H NMR spectrum shows equilibration of the two methyl groups of 4,6-dimethylpyrimidinethiol, as well as equilibration between free and complexed ligand, since only two resonances at δ 6.97 and 2.35 ppm are observed, assignable to the aromatic and methyl proton resonances, respectively. Further additions of 4,6-dimethylpyrimidinethiol to the DMSO solution of **1** lead to gradual shifts of the ligand resonances toward their uncomplexed values. At a free ligand:**1** ratio of 2:1, a new complex is isolated that is identified as Au(4,6-Me_2pym-2-S)(4,6-Me_2pymH-2-S), **2**, as in eq 1. The structure of **2**[24] reveals a nearly linear S−Au−S coordination and a crystal structure having N−H···N hydrogen bonds between 4,6-Me_2-pyrimidinethiol and -thiolate ligands on adjacent molecules with no evidence of aurophilic interactions (nearest Au···Au, 6.962(1) Å).



(1)

For both **1** and **2** in DMSO solution, an intense absorption band at ca. 290 nm (ϵ = 23 270 and 15 050 $dm^3\ mol^{-1}\ cm^{-1}$, respectively) and a weak band at ca. 360 nm (ϵ = 2750 and 1090 $dm^3\ mol^{-1}\ cm^{-1}$) are seen. These two bands are also seen in the absorption spectrum of the free ligand. Compound **1** also possesses an absorption at 335 nm (ϵ = 5970 $dm^3\ mol^{-1}\ cm^{-1}$) that may correspond to a metal-centered transition involving Au_2.[25] Dimer **1** is brightly luminescent in the solid state with a broad asymmetric emission maximizing at 516 nm. Corresponding emission spectra in room temperature fluid solutions and 95 K rigid glasses give clear evidence of aggregation effects.[26,27] This is illustrated in Figure 2A for fluid solution emission as a function of concentration. Two emission maxima are noted at 416 and 532 nm, with the latter absent at 2×10^{-6} M and dominating at concentrations greater than 6×10^{-5} M. The energy of the latter band also shifts with concentration from 518 nm at 3×10^{-5} M to 532 nm at 1×10^{-4} M. A similar observation is seen in frozen DMSO solutions at 95 K with emission maxima at 428 and ca. 570 nm, the latter of which shifts to lower energy with increasing concentration and is the major feature at higher concentrations (Figure 2B). The higher energy emission undoubtedly corresponds to an intraligand ($\pi\pi^*$ or $n\pi^*$) state or to a Au(I)-to-π^*-(pyrimidine) charge transfer. Support for this view comes from the luminescence of the mononuclear complex **2** and related systems.[28] Compound **2** is strongly emissive in frozen DMSO, showing a broad emission with λ_{max} at 427 nm upon photoexcitation between 280 and 360 nm; in room temperature fluid solution, it is nonemissive. The lower energy emission from **1** is thought to occur from a Au_2 excited state similar to those proposed previously.[18,20,27,29−32] The shift in λ_{max} for this band suggests that this feature is influenced by aggregation. While such effects have been associated with intermolecular aurophilic interactions leading to the formation of oligomers joined along Au···Au chains, the presence of the 4-methyl groups in **1** should inhibit that.[4,5,26,27] Accordingly, we propose that in the case of the 4,6-dimethylpyrimidinethiolate dimer **1**, aggregation effects result from π stacking. This feature, while often observed in planar unsaturated systems, is unique for Au(I) complexes.

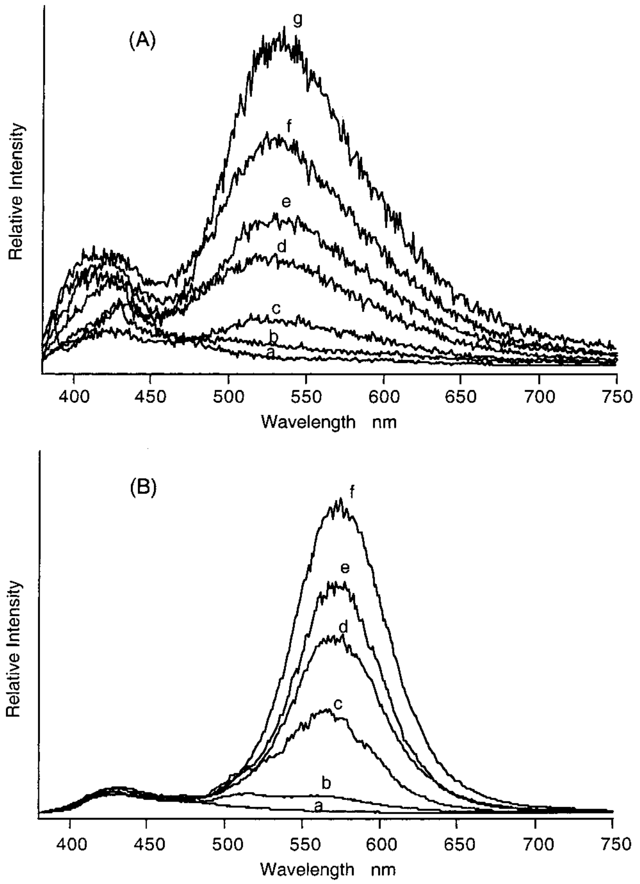


Figure 2. (A) Emission spectra of **1** in DMSO as a function of concentration (M) at ambient temperature: (a) 2×10^{-6}; (b) 2×10^{-5}; (c) 3×10^{-5}; (d) 4×10^{-5}; (e) 6×10^{-5}; (f) 1×10^{-4}; (g) 2×10^{-4} M. (B) Emission spectra at 95 K in DMSO: (a) 2×10^{-6}; (b) 6×10^{-6}; (c) 2×10^{-5}; (d) 4×10^{-5}; (e) 6×10^{-5}; (f) 1×10^{-4} M with excitation at 330 nm.

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Supporting Information Available: Tables of crystallographic data, positional parameters, and bond lengths and angles for **1**·DMSO and **2**; packing diagram for **1**·DMSO; ORTEP drawing for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Crystal data for **2**: monoclinic, space group $P2_1/n$, $a = 7.5642(2)$ Å, $b = 14.5318(3)$ Å, $c = 13.1829(3)$ Å, $\beta = 90.83(1)°$, $V = 1448.93(6)$ Å^3, $Z = 4$, temp = 193(2) K, Siemens SMART diffractometer, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $4.2° < 2\theta < 56.7°$, 8621 measd data, 3369 unique, 2638 obsd with $I > 2\sigma(I)$, full-matrix F^2 refinement, R1 = 0.029, wR2 = 0.058 (all data).

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