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Multiple Emissions and Brilliant White Luminescence from Gold(I) *O,O′*-Di(alkyl)dithiophosphate Dimers

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Luminescence is a prominent property of Au(I) compounds in the solid state, as well as in rigid media at low temperatures. For these systems, understanding their emission and tuning their excited-state properties are essential for their eventual use as luminescent sensors and dopant emitters in OLED applications.[1−4] The luminescent state in Au(I) dimers and in aggregated structures exhibiting aurophilic interactions has generally been assigned to the metal-centered (MC) $^3(d_{z^2}\sigma^* \rightarrow p_z\sigma)$ state in close parallel with that attributed to Pt(II), Rh(I), and Ir(I) d^8 square planar complexes.[5−11] As a consequence of aurophilic interactions, Au(I) dimers are often found to have solid-state structural arrangements possessing one-dimensional Au···Au chains, but the luminescence from these systems often shows a poor correlation between λ_{em} and intra- and intermolecular Au···Au separations.[8,9] Within the last five years, a number of new and interesting developments have been reported including "solvo-luminescence" from solid samples of the trinuclear complex $\{Au_3(\mu\text{-MeN}{=}COMe)_3\}$ and reversible switching on-and-off of luminescence for $Au_2\{S_2CN(C_5H_{11})_2\}_2$ by exposure to volatile organic vapors.[12−14] Recently, Balch et al. have described a dramatic variation in emission color of the Au(I) diaminocarbene complex $[Au\{C(NHMe)_2\}_2](PF_6)$ in frozen solutions of different solvents.[15] In the present study, we report the structures of several Au(I) dimers and their luminescence properties that include multiple emissions, bright white solid-state luminescence, and, as seen for the diaminocarbene complex, brilliant emissions of different color from different frozen glasses. The multiple emitting states include both ^{1}MC and ^{3}MC states, representing the first time that the former has been identified as such, and a lower energy $^3(\text{S p} \rightarrow \text{Au } p_z\sigma)$ ligand-to-metal charge transfer (LMCT).

The Au(I) complexes $Au_2\{S_2P(OR)_2\}_2$ (R = Me, Et, *n*-Pr, *n*-Bu) are prepared by the reaction of $AuCl(SMe_2)$ with stoichiometric amounts of $KS_2P(OR)_2{\cdot}2H_2O$ in dichloromethane to give colorless to pale yellow needle crystals in high yield. The resultant, analytically pure $Au_2\{S_2P(OR)_2\}_2$ dimers have been characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopies, and for the R = Me and Et derivatives, single-crystal structure determinations have been performed.[16−18] The structures are similar to that of the *i*-propyl derivative, $Au_2\{S_2P(O\text{-}i\text{-}Pr)_2\}_2$, reported previously.[19] Figure 1 shows the structure of $Au_2\{S_2P(OMe)_2\}_2$ with shorter inter- and longer intramolecular Au···Au distances of 3.094(1) and 3.177(1) Å forming gold chains along the *c* axis of the crystal and nearest neighbor dimers rotated by ca. 83° along the Au···Au direction to minimize nonbonding repulsions between adjacent ligands. The Et derivative possesses a similar structure, albeit with variation in the Au···Au inter- and intramolecular distances (inter: 3.162(1), 3.082(1) Å; intra: 3.131(1), 3.102(1), 3.186(1) Å). All of the Au···Au distances indicate substantial aurophilic interactions.[20−22]

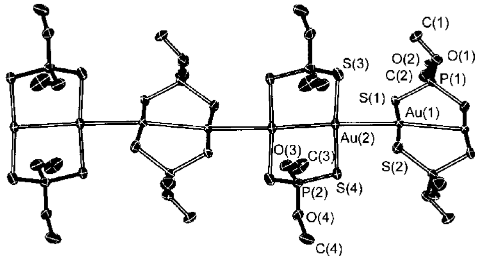

Figure 1. Perspective view of $Au_2\{S_2P(OMe)_2\}_2$. Selected interatomic distances (Å) and angles (deg): Au(1)−Au(2), 3.0940(10); Au(1)−Au(1)-#1, 3.1758(13); Au(2)−Au(2)#2, 3.1786(14); S(2)−Au(1)−S(1), 173.16(16); S(4)−Au(2)−S(3), 173.34(19); Au(2)−Au(1)−Au(1)#1, 171.39(4); Au(1)−Au(2)−Au(2)#2, 159.66(5). Designations #1 and #2 correspond to the symmetry transformations $1 - x$, $1 - y$, $1 - z$ and $1 - x$, $1 - y$, $2 - z$, respectively.

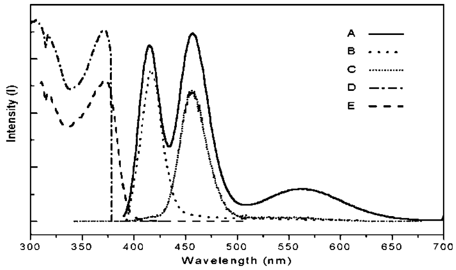

Figure 2. Emission and excitation spectra of $Au_2\{S_2P(OMe)_2\}_2$ at 77 K in the solid state mixed with KBr: (A) emission, $\lambda_{ex} = 365$ nm; (B) 20 ns component; (C) 2.2 μs component; (D) excitation, $\lambda_{em} = 415$ or 460 nm; (E) excitation, $\lambda_{em} = 565$ nm.

In the solid state using pure polycrystalline samples, $Au_2\{S_2P(OMe)_2\}_2$ and, to a lesser extent, the Et derivative exhibit white luminescence which becomes brilliant at 77 K. The 298 K emission spectrum of $Au_2\{S_2P(OMe)_2\}_2$ shows a λ_{em} max of 422 nm and a long emission tail extending throughout the visible region (see Supporting Information). The Et derivative possesses a similar emission spectrum, while the *n*-Pr complex shows a broad emission centered at 620 nm as well as a higher energy emission at 436 nm. The 77 K emission spectra of the complexes reveal three bands for each in different relative amounts. For $Au_2\{S_2P(OMe)_2\}_2$, the maxima are at 415, 456, and 560 nm with the first two bands more intense (see Figure 2). Time-resolved measurements reveal that the highest energy band at 415 nm has a lifetime of ca. 20 ns, whereas the second band at 456 nm possesses a 2.2 μs lifetime, corresponding to fluorescence and phosphorescence, respectively (Figure 2).

Further investigation into the nature of the emission from $Au_2\{S_2P(OMe)_2\}_2$ probed the notion of aggregation as a contributing factor. Samples of the complex in dichloromethane solutions of widely varying concentrations were spotted onto an inert paper support followed by solvent evaporation, immersion in liquid N_2,

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and emission measurement. For samples made from concentrations greater than 1.0 × 10^{-3} M, all three bands were observed in emission spectra, and the samples exhibited bright white luminescence, whereas for samples made from more dilute solutions, the higher energy emissions were greatly attenuated, and the overall emission was orange (see Supporting Information). These results indicate that the *higher* energy bands of $Au_2\{S_2P(OMe)_2\}_2$ have a concentration dependence consistent with aggregate-based excited states, while the lowest energy band is dimer localized. Qualitatively similar emission results were obtained for the Et derivative.

Assignment of the emission bands for $Au_2\{S_2P(OMe)_2\}_2$ can be made on the basis of reports for Au(I) thiolate compounds in which a filled nonbonding S p orbital is considered to reside energetically between the Au $d_{z^2}\sigma^*$ and $p_z\sigma$ functions that are respectively filled and vacant.[8,23] This ordering indicates that a ligand-to-metal charge transfer (LMCT; S $p\pi \rightarrow$ Au $p_z\sigma$, or for an aggregated system, LMMCT[3]) should be expected at lower energy than the metal-centered (MC) excited states ($d_{z^2}\sigma^* \rightarrow p_z\sigma$) usually invoked for Au(I) complexes exhibiting aurophilic interactions. On the basis of the lifetime measurements, we assign the higher energy emission bands at 415 and 456 nm to ^{1}MC and ^{3}MC states, respectively, and the broad band at 560 nm to the ^{3}LMCT state. While assignments of emission in Au(I) compounds have been made most often to ^{3}MC states, the corresponding ^{1}MC emission has been noted only once before (on the basis of unreported solution lifetimes),[24] and emission from both MC states in the same sample has not been reported previously. Analogous fluorescence and phosphorescence bands appear to have been seen for $[Au\{C(NHMe)_2\}_2](PF_6)$ on the basis of time-correlated emission spectra, but assignments were not made,[15] and for the related complexes $Au_2\{S_2PPh(OR)\}_2$ by van Zyl et al., an LMCT assignment was proposed instead with no lower energy band observed.[25]

The $Au_2\{S_2P(OR)_2\}_2$ complexes are not emissive in fluid solutions of different solvents, but luminescence is seen when the solutions are cooled and becomes brilliant when the solutions are frozen. Moreover, the emission is of different color in different solvents and exhibits striking thermochromism. The emission spectra of $Au_2\{S_2P(OMe)_2\}_2$ and its Et analogue in various frozen glasses at 77 K are shown in Supporting Information. Only a single higher energy MC emission is seen in these spectra around 440 nm, and it possesses a lifetime of 30 ns in a toluene glass. The lower energy LMCT emission occurs at 600 nm in the same sample, and its lifetime is found to be 9.2 μs. Differences in the relative magnitudes of the higher and lower energy bands lead to clear differences in the colors of the frozen glass samples obtained from the different solvents. For example, $Au_2\{S_2P(OMe)_2\}_2$ in frozen toluene exhibits orange emission, whereas in methylene chloride it is violet. The thermochromism is evident when 77 K samples are allowed to warm slowly, yielding a striking progression of color. For $Au_2\{S_2P(OMe)_2\}_2$ in frozen toluene glass, the color changes from orange to bright yellow and green before eventually disappearing on warming. Finally, for any one sample, the emission varies as the excitation wavelength changes with the higher energy band shifting by 3−5 times that of the lower energy band in cm^{-1}. For example, excitation of $Au_2\{S_2P(OMe)_2\}_2$ at 325 nm results in emission bands with λ_{max} at 422 and 595 nm, while excitation at 365 nm results in emission with λ_{max} at 440 and 601 nm. Emission and excitation spectra from $Au_2\{S_2P(OMe)_2\}_2$ in different frozen glasses are given in Supporting Information.

The different emission colors and the thermochromism of the luminescence in frozen glass media result from changes in both the aggregate size of aurophilically linked oligomers and the relative intensities of emission from the two bands. Variation of emission maxima with λ_{ex} and the corresponding variation of excitation bands measured at different λ_{em} are consistent with different degrees of association in the various glass media, leading to the observed colors in the various glasses. Careful control of the factors determining the extent and dynamics of Au_2L_2 aggregation and the relative intensity of each emission band in these Au(I) systems is a current research objective.

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Supporting Information Available: X-ray crystallographic data in CIF format and printable tables for $Au_2\{S_2P(OMe)_2\}_2$ and $Au_2\{S_2P(OEt)_2\}_2$, and analytical, spectroscopic, and photophysical data for $Au_2\{S_2P(OR)_2\}_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Spectroscopic and analytical data are given in Supporting Information
(17) X-ray data were collected at 193 K on a standard Siemens SMART CCD diffractometer with Mo Kα radiation. Structure solutions were obtained by standard Patterson and difference Fourier methods and refined on F^2. $Au_2\{S_2P(OMe)_2\}_2$: $a = 6.9799(10)$ Å, $b = 9.5144(13)$ Å, $c = 12.3951(18)$ Å, $\alpha = 105.365(2)$ deg, $\beta = 97.975(2)$ deg, $\gamma = 103.545(3)$ deg, $V = 753.74(19)$ Å^3, triclinic $P1$(bar), $Z = 2$, $\theta_{min/max} = 1.74/23.24$ deg, 2162 unique observed reflections were used to refine 146 atomic parameters and gave a final R factor of 0.0652. $Au_2\{S_2P(OEt)_2\}_2$: $a = 8.3143(7)$ Å, $b = 9.4747(8)$ Å, $c = 24.851(2)$ Å, $\alpha = 100.182(2)$ deg, $\beta = 90.635(2)$ deg, $\gamma = 95.133(2)$ deg, $V = 1918.3(3)$ Å^3, triclinic $P1$(bar), $Z = 2$, $\theta_{min/max} = 1.67/25.00$ deg, 6719 unique observed reflections were used to refine 361 atomic parameters and gave a final R factor of 0.0884.
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