J. Am. Chem. Soc. **1998,** *120,* 1329−1330

Linear Chain Au(I) Dimer Compounds as Environmental Sensors: A Luminescent Switch for the Detection of Volatile Organic Compounds

M. Adnan Mansour,[†,‡] William B. Connick,[‡]
Rene J. Lachicotte,[‡] Henry J. Gysling,[†,§] and
Richard Eisenberg*,[†,‡]

Science and Technology Center for
Photoinduced Charge Transfer and Department of Chemistry
University of Rochester, Rochester, New York 14627
Imaging Research and Advanced Development
Eastman Kodak Company, Rochester, New York 14650

Received September 12, 1997

The efficient monitoring of volatile organic compounds (VOCs) has gained prominence in environmental and public safety control due to the potential health hazards posed by exposure to these substances. Indeed, the development of robust and well-defined sensors for the detection of VOCs has become the subject of intensive study.[1−4] The use of metal complexes as O_2,[5−8] CO_2,[9,10] pH,[11,12] and metal ion[13] sensors has been investigated extensively, but their use as optical sensors for VOC detection has not been exploited until fairly recently. In 1995, Mann and co-workers[14] reported that the double salts $[PtL_4][M(CN)_4]$ (L = arylisonitrile; M = Pt, Pd) having structures composed of stacked square planar complexes are spectroscopically sensitive to the presence of VOC vapors with films exhibiting shifts in absorption and emission maxima (vapochromism) characteristic for specific organic solvents.[15] More recently, Balch and co-workers[16] have observed that, when a colorless trimeric Au(I) complex is irradiated with long-wavelength UV light, subsequent contact with solvent results in an intense yellow luminescence. In both the Pt double salts and the trinuclear Au(I) system, the emission is due to an excited-state arising from intermolecular metal−metal interactions.

In this communication, we report the reversible interaction of a dimeric gold(I) dithiocarbamate complex, $[Au(S_2CN(C_5H_{11})_2)]_2$ (**1**), with VOC vapors that results in both a dramatic color change and a positive "switching on" of luminescence. It is known that dithiocarbamate complexes of Au(I), as well as other Au(I) dimers containing P and C donor bridging ligands, possess a strong propensity to aggregate and form chains with short intermolecular Au···Au contacts.[17,18] On the basis of theoretical and spectroscopic investigations, the nature of these interactions has been analyzed by Fackler and co-workers,[18] who assigned the solid-state luminescence of Au(I) dimers as due to either $(d\sigma^*)^1(p\sigma)^1$ or $(d\delta^*)^1(p\sigma)^1$ excited states. In the present study, the observation of luminescence occurs *only* on exposure of **1** to VOCs. In their absence, the emission is completely quenched. Single-crystal structural studies of **1** in both luminescent and nonemissive forms underscore the necessity of *inter*molecular Au···Au interactions in order to observe photoluminescence.

Complex **1** was prepared by a slight modification of the literature method.[19] Addition of 2 equiv of $KS_2CN(C_5H_{11})_2$ in water to a solution of "$AuCl_2^-$" generated in situ by the addition of Na_2SO_3 to a NaCl-saturated aqueous solution of $K[AuCl_4]$ affords **1** in ca. 50% yield after recrystallization from acetone. The complex was characterized by ^1H NMR and IR spectroscopies and mass spectrometry and found to be analytically pure by elemental analysis.[20] The bright orange microcrystalline compound, **1**·solvate, exhibits intense luminescence when exposed to UV light (366 nm). However, upon drying in air for several days or in vacuo for several hours, the solid becomes colorless and nonemissive. If the resultant solid is exposed to vapors of polar aprotic solvents, e.g., acetone, CH_3CN, CH_2Cl_2, and $CHCl_3$, it becomes orange again and regains its emissive property; this effect is not observed with protic solvents such as MeOH and EtOH. The process is fully reversible as demonstrated through numerous cycles without any decomposition of the material as evidenced by ^1H NMR spectroscopy. The emission spectrum of the orange solid at room temperature is composed of a broad band centered at 631 nm.[21] At 77 K, this band sharpens and shifts to higher energy (604 nm).

Single crystals of both the colorless and orange forms of **1** have been structurally characterized by X-ray diffraction.[22] The molecular structures are similar, with bridging dithiocarbamates and an approximately linear S−Au−S coordination geometry, and closely resemble those reported for other gold(I) dithiocarbamate complexes.[23−25] Crystals of orange, luminescent **1**·DMSO are composed of discrete dimers stacked along the *c* axis to form an infinite chain of Au atoms (Figure 1) with short intermolecular Au···Au contacts (2.9617(7) Å). Consecutive dimers along the chain are rotated by approximately 90°, resulting in a staggered

---

[†] Science and Technology Center for Photoinduced Charge Transfer, University of Rochester.

[‡] Department of Chemistry, University of Rochester.

[§] Eastman Kodak Company.

(1) Wells, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3988−3989.

(2) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27−34.

(3) Hierlemann, A.; Bodenhoefer, K.; Fluck, M.; Schurig, V.; Goepel, W. *Anal. Chim. Acta* **1997**, *346*, 327−339.

(4) Menon, A.; Haimbodi, M.; Zhou, R.; Jose, F. *Electron. Lett.* **1997**, *33*, 287−289.

(5) Xu, W.; Kneas, K. A.; Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1996**, *68*, 2605−2609.

(6) Di Marco, G.; Lanza, M.; Pieruccini, M.; Campagna, S. *Adv. Mater.* **1996**, *8*, 576−580.

(7) Chuang, H.; Arnold, M. A. *Anal. Chem.* **1997**, *69*, 1899−1903.

(8) Mills, A.; Lepre, A.; Theobald, B. R. C.; Slade, E.; Murrer, B. A. *Anal. Chem.* **1997**, *69*, 2842−2847.

(9) Li, P. C. H.; Thompson, M. *Analyst* **1994**, *119*, 1947−1951.

(10) Egashira, N.; Kumasako, H.; Kurauchi, Y.; Ohga, K. *Anal. Sci.* **1994**, *10*, 405−408.

(11) de Silva, A. P.; Gunaratne, H. Q. N.; Rice, T. E. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2116−2118.

(12) Badr, I. H. A.; Meyerhoff, M. E.; Hassan, S. S. M. *Anal. Chem.* **1995**, *67*, 2613−2618.

(13) Seitz, W. R.; Zhujun, Z.; Mullin, J. L. *Proc. SPIE−Int. Soc. Opt. Eng.* **1987**, *713*, 126−131.

(14) Exstrom, C. L.; Sowa, J. R., Jr.; Daws, C. A.; Janzen, D.; Mann, K. R. *Chem. Mater.* **1995**, *7*, 15−17.

(15) Daws, C. A.; Exstrom, C. L.; Sowa, J. R. J.; Mann, K. R. *Chem. Mater.* **1997**, *9*, 363−368.

(16) Vickery, J. C.; Olmstead, M. M.; Fung, E. Y.; Balch, A. L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1179−1181.

(17) Che, C.-M.; Wong, W.-T.; Lai, T.-F.; Kwong, H.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 243−244.

(18) King, C.; Wang, J.-C.; Khan, M. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145−2149.

(19) Miller, J. B.; Burmeister, J. L. *Synth. React. Inorg. Met.-Org. Chem.* **1985**, *15*, 223−233.

(20) ^1H-NMR (benzene-d_6): δ 3.47 (t, 8H), 1.53 (m, 8H), 1.15 (quin., 8H), 0.99 (quin., 8H), 0.84 (t, 12H). IR (KBr): ν(CN) 1488 (s) cm^{-1}; ν(CS) 968 (sh), 950 (m) cm^{-1}. MS: *m/z* 858 (M^+), 661 ($M^+ - Au$). Anal. Calcd for $C_{22}H_{44}Au_2N_2S_4$: C, 30.77; H, 5.16; N, 3.26. Obsd: C, 30.70; H, 4.80; N, 3.18.

(21) The emissions from crystalline samples of **1**·DMSO exhibit biexponential decays that are dependent on sample history ($\tau_1 = 60 - 100$ ns, $\tau_2 = 260−400$ ns).

(22) Orange crystals (**1**·DMSO) were grown from CH_2Cl_2/DMSO, colorless crystals (**1**) from *n*-PrOH/benzene, and orange crystals (**1**·CH_3CN) from benzene/CH_3CN. 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. Crystallographic data are given as *a*, *b*, *c* (Å); α, β, γ (deg); space group, *Z*, $2\theta_{min/max}$, no. of unique data, R_1/Rw (%). **1**·DMSO: 18.4187(1), 30.1985(6), 11.4563(2); 90, 96.974(1), 90; $P2_1/c$, 8, 3.5°/45.6°, 8595, 6.10/8.64. **1**: 10.3867(1), 13.2244(1), 11.3223(2); 90, 107.219(1), 90; *Pn*, 2, 4.6°/56.5°, 5165, 2.93/6.60. **1**·CH_3CN: 28.96040(10), 11.6285(2), 18.7224(3); 90, 90, 90; *Pbcn*, 8, 2.82°/45.0°, 4098, 7.47/16.69.

(23) Hesse, R.; Jennische, P. *Acta Chem. Scand.* **1972**, *26*, 3855−3864.

(24) Jennische, P.; Anacker-Eickoff, H.; Wahlberg, A. *Acta Crystallogr.* **1975**, *31*, S143−S144.

(25) Heinrich, D. D.; Wang, J.-U.; Fackler, J. P. *Acta Crystallogr.* **1990**, *C46*, 1444−1447.

S0002-7863(97)03216-2 CCC: $15.00

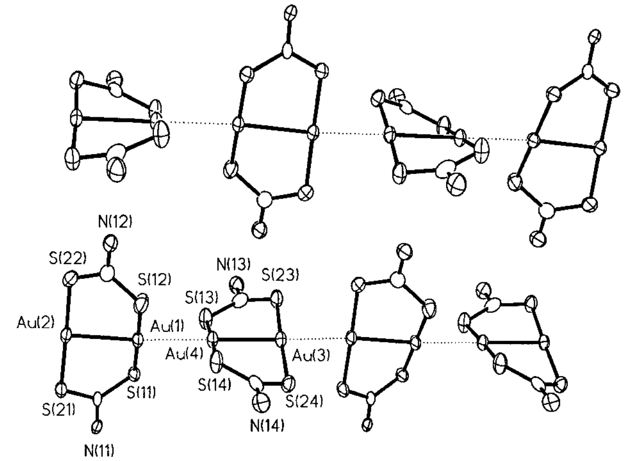

Figure 1. Drawing of the $[Au(S_2CN(C_5H_{11})_2)]_2$ molecule in the structure of **1**·DMSO with two repeat units of chains in the structure viewed perpendicular to the stacking axis. Thermal ellipsoids are drawn at the 50% probability level. The pentyl moieties have been omitted for clarity.

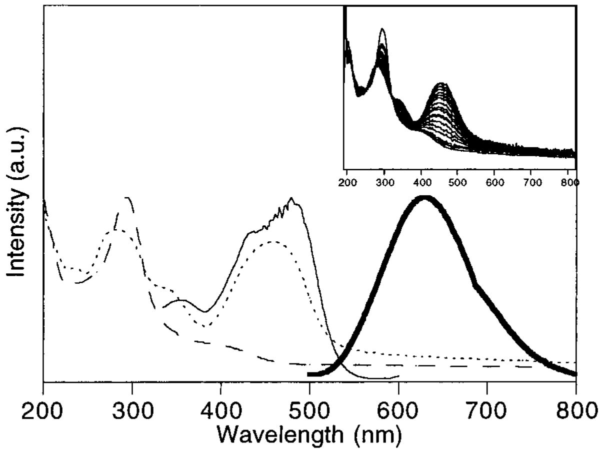

Figure 2. UV−vis absorption (···), emission (bold line) (λ_{ex} = 460 nm), and excitation (—) (λ_{em} = 630 nm) spectra at room temperature of an orange CH_2Cl_2 cast film of $[Au(S_2CN(C_5H_{11})_2)]_2$ (**1**) on a quartz disk; absorption spectrum (− −) of dry film of **1**. Inset: Absorption spectra of dry **1** upon direct exposure to acetone vapor for 15- or 30-s intervals.

arrangement. While the intramolecular Au−Au distance of 2.7690(7) Å agrees with those in other gold dithiocarbamate dimers, the intermolecular Au···Au separation is the shortest thus far observed in these systems. A solvent of crystallization, having less than full occupancy, shows no direct interaction with the Au centers. The same structural pattern exists in crystals grown from acetonitrile with slightly longer inter- and intramolecular Au···Au distances of 3.0241(12) and 2.7916(12) Å, respectively. The structure of the colorless, nonemissive form shows that the dimers exist as discrete, noninteracting molecular units with a shortest intermolecular Au···Au distance of 8.135 Å. The intramolecular Au−Au distance of 2.7653(3) Å is nearly identical to that in the orange form. Clearly, these results point to the formation of linear Au···Au chains induced by solvent as a key to the orange color and luminescence of **1**, even though there is no unusual interaction between the solvent and the complex in the solid. Only a fraction of an equivalent of solvent relative to complex is required to induce aggregation. By NMR integration of **1**·acetone dissolved in benzene-d_6, one solvent molecule exists per 2.5 dimers, while from thermogravimetric analysis, the observed weight loss corresponds to one acetone molecule per three dimers.

To probe further the optical properties of **1**, films were prepared by spin-coating a CH_2Cl_2 solution of the complex onto 2.5-cm quartz disks. As shown in Figure 2, the orange films saturated with CH_2Cl_2 exhibit intense emission at 630 nm upon excitation at the absorption maximum of 460 nm. When the film and disk support are heated at 50 °C for 10 s, the orange color fades and the resultant pale yellow film is nonemissive. The absorption spectrum of the dry film exhibits a low-energy shoulder near 410 nm and a prominent UV band at 294 nm (281 nm in the orange film). The absorption and emission maxima of the films show little variation with different solvents. For example, the acetone- and acetonitrile-containing films exhibit maxima at 465 and 461 nm, respectively, and emission maxima at 624 and 626 nm (λ_{ex} = 460 nm). The dried films for all solvates have virtually identical spectra. When the dry film is exposed to acetone vapor for 15-s intervals, the high-energy band (294 nm) isosbestically splits into two features at 284 and 331 nm (sh) with the concomitant emergence of a peak at 465 nm (Figure 2, inset). Subsequent drying of this film regenerates the original spectrum. Upon exposure of the dry film to CH_2Cl_2 vapor at its equilibrium vapor pressure in a closed chamber for 10 min, the film regains its orange color and emissive property. While the absorption spectrum is qualitatively consistent with that of the original film, the absorbance is somewhat diminished. Repetitive cycling results in further reduction in absorbance of the dry and solvated films as a result of film degradation. We find no evidence of chemical degradation as the ^1H NMR spectrum of the film redissolved in benzene-d_6 after five cycles is virtually identical to that obtained from the initial material, with no additional resonances. Furthermore, the cycled film can be dissolved and recast to give a film with properties comparable to those of the original film.

The requirement for aggregation in order to observe luminescence is further supported by absorption and emission studies of **1** in fluid solution and rigid media. Whereas the dilute, colorless solutions are not emissive, a concentrated (2×10^{-2} M), yellow solution of **1** in degassed CH_2Cl_2 is weakly emissive with λ_{max} at 515 nm and a long tail extending to 700 nm, consistent with varying degrees of oligomerization or aggregation in solution. Indeed, deviation from Beer's Law at high concentrations ($>5 \times 10^{-3}$ M) of **1** in benzene is consistent with aggregation in fluid solution. When films of **1** in poly(methyl methacrylate) or polycarbonate at 5−10% w/w complex/polymer are irradiated, no emission is observed, in accord with the notion that the complex is dispersed evenly throughout the inert polymer matrix. In contrast, an intense and very broad emission at 563 nm (λ_{ex} = 460 nm) is observed from a dilute (6×10^{-6} M) 77 K 1:1:1 DMF:MeOH:CH_2Cl_2 glass, suggesting aggregate formation upon glassing. This emission is found to be wavelength-dependent with higher energy emission seen for higher energy excitation. For example, excitation at 410 nm results in emission with λ_{max} near 540 nm while excitation at 500 nm yields emission with λ_{max} near 580 nm. It is conceivable that there exists a distribution of aggregates (in the glass) with longer chains of Au complexes absorbing and emitting at longer wavelengths than shorter chains. The mechanism by which solvent vapor induces the observed effects is under continuing study.

Acknowledgment. We thank the National Science Foundation (Grant CHE 9120001) Center for Photoinduced Charge Transfer for support of this work.

Supporting Information Available: X-ray crystallographic reports for **1**, **1**·DMSO, and **1**·MeCN (27 pages). See any current masthead page for ordering and Web access instructions.

JA973216I