Inorg. Chem. **2004**, *43*, 3833–3839

Inorganic Chemistry
Article

Synthesis, Characterization, and Luminescent Properties of Dinuclear Gold(I) Xanthate Complexes: X-ray Structure of [$Au_2(^n$Bu-xanthate$)_2$]

Ahmed A. Mohamed, Ibrahim Kani, Anna O. Ramirez, and John P. Fackler, Jr.*

*Laboratory for Molecular Structure and Bonding, Department of Chemistry,
Texas A&M University, College Station, Texas 77843-3255*

Received August 19, 2003

The synthesis and characterization of gold(I) complexes of butyl xanthate [$Au_2(^n$Bu-xanthate$)_2$], **1**, and ethyl xanthate [Au_2(Et-xanthate$)_2$], **2**, are described. These complexes are readily prepared from the reaction between Au(THT)Cl (THT = tetrahydrothiophene) and the corresponding xanthate ligands as the potassium salts. The two xanthate complexes are characterized by ^{1}H NMR, IR, mass spectrometry, elemental analysis, and UV–vis techniques. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) show that the gold xanthate complexes decompose to yield mainly gold metal at ∼200 °C, confirmed by X-ray powder diffraction. Excitation of the complexes at 450 nm in the solid state at 77 K produces a strong red emission at ca. 690 nm with a broad asymmetric profile tailing to 850 nm. The dinuclear gold(I) xanthate complex, [$Au_2(^n$Bu-xanthate$)_2$], **1**, is the first structurally characterized binary Au(I) xanthate. The Au···Au distance in the eight-membered ring is 2.8494(15) Å while the shortest intermolecular Au···Au interaction between independent units is 3.64 Å. The angle between the planes containing the molecules in the unit cell is ∼69.56°. The light green plates of [$Au(\mu$-$S_2COBu^n)]_2$ crystallize in the orthorhombic space group $P2_12_12$ with $a = 37.254(14)$ Å, $b = 7.287(3)$ Å, $c = 6.054(2)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, and $V = 1643.4(11)$ Å^3.

Introduction

Xanthates were first discovered by Zeise[1] in 1822 and have been used by industry as flotation agents for the thiophilic minerals of the transition metals such as copper, zinc, cobalt, nickel, and gold.[2] They have been used widely as reagents for the separation and quantitative determination of a large number of cations. Xanthates of a few of the transition metals have been prepared in recent years to determine their composition and structure.[3] The trifluoroethyl xanthate has been used as a reagent for the analytical determination of gold.[3d]

The photophysics of d^{10} gold(I) complexes has attracted considerable attention over the past few years.[4] The relationship between the presence of weak intermolecular bonding interactions between neighboring gold centers and emission from dinuclear gold(I) thiolates has been implicated in the design of electronic and sensor devices.[5] Recently a gold(I) dithiocarbamate has been found to be a luminescent switch for the detection of volatile organic compounds (VOC's).[5b,6] Recent work in our laboratory[7] established that gold(I) dithiophosphonate complexes, $Au_2[S_2P(OR)R']_2$, form an interesting modification of the known dithiophosphate chemistry.[8] The asymmetric nature of the ligand allows for cis and trans isomers to be formed, a feature not possible for the symmetrical dithiophosphinates, $[S_2PR_2]^-$, or dithiophosphates, $[S_2P(OR)_2]^-$.[9]

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* Author to whom correspondence should be addressed. E-mail: fackler@mail.chem.tamu.edu.

(1) Zeise, W. C. *Ann. Pharm.* **1835**, *16*, 178.

(2) (a) Rao, S. R. *Xanthates and related compounds*; Marcel Dekker: New York. 1971. (b) Han, K. N.; Meng, X. U.S Patent 5114687, 1992; 5 pp. (c) Wing, R. E.; Doane, W. M. U.S. Patent 695617, 1976; 37 pp. (d) Coucouvanis, D. *Prog. Inorg. Chem.* **1979**, *26*, 302.

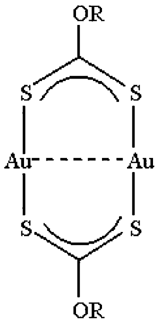
(3) (a) Exarchos, G.; Robinson, S.; Steed, J. *Polyhedron* **2001**, *20*, 2951. (b) Cox, M. J.; Tiekink, E. R. *Z. Kristallog.* **1996**, *211*, 753. (c) Vastag, S.; Marko, L.; Rheingold, A. L. *J. Organomet. Chem.* **1990**, *397*, 231. (d) Moran, M.; Cuadrado, I.; Masaguer, J. R.; Losada, J.; Foces-Foces, C.; Cano, F. H. *Inorg. Chim. Acta* **1988**, *143*, 59. (e) Moran, M.; Cuadrado, I.; Munoz-Reja, C.; Masaguer, J. R.; Losada, J. *J. Chem. Soc., Dalton Trans.* **1988**, 149. (f) Moran, M.; Cuadrado, I.; Masaguer, J. R.; Losada, J. *J. Organomet. Chem.* **1987**, *335*, 255. (g) Hussain, M..F.; Bansai, R. K.; Puri, B. K.; Satake, M. *Analyst* **1984**, *109*, 1151.

(4) (a) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum Press: New York, 1994. (b) Che, C. M.; Kwong, H. L.; Poon, C. K.; Yam, V. W. W. *J. Chem. Soc., Dalton Trans.* **1990**, 3215. (c) Li, D.; Che, C. M.; Kwong, H. L.; Yam, V. W. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3325. (d) Jaw, H. R. C.; Savas, M. M.; Rogers, R. D.; Mason, W. R. *Inorg. Chem.* **1989**, *28*, 1028. (e) Hong, X.; Cheung, K. K.; Guo, C. X.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 1867. (f) Forward, J. M.; Fackler, J. P., Jr.; Assefa, Z. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M.; Fackler, J. P., Jr., Eds.; Plenum Press: New York, 1999; p 195.

10.1021/ic0349858 CCC: $27.50

A related class of Au(I) compounds that has received substantial study is ylides, $Au_2[(CH_2)_2PRR']_2$. These materials are known to undergo oxidative-addition to stable dinuclear Au(II) and Au(III) products as well as mixed-valence species. Comprehensive reviews of this chemistry are available.[10]

Surprisingly little is known, however, about Au(I) xanthates (see sketch). Potassium xanthates are synthesized by saturating the corresponding alcohol with potassium hydroxide followed by adding carbon disulfide. Like the dithiocarbamates[2] formed from amine reactions with CS_2, the delocalized electronic structure of this class of compounds has led to many interesting and significant metal-containing compounds. The reason for the lack of study of gold xanthates appears to be related to questions of stability and the malodorous decomposition products produced. Since the R group influences the stability of xanthates and related dithiolates, our efforts initially have been directed to the synthesis of a dinuclear xanthate with an R group sufficiently long to reduce volatility yet short enough to allow crystallization. Studies of the nickel(II) alkyl xanthates, $Ni(S_2COR)_2$, had nicely demonstrated these features.[11]



Dinuclear gold(I) xanthate; R = Et, n-Bu

A few studies of gold xanthate complexes have been done with Au(III) and Au(I). This work includes well-characterized compounds such as $[(PPh_3)_2AuS_2COEt]$, $(CEP)_2AuS_2COR$ (CEP = tris(cyanoethyl)phosphine; R = Me, Et, Bu),[12] the organometallic[13] $[(CH_3)_2AuS_2CO\text{-}2,6\text{-}C_6H_3(CH_3)_2]$ and related xanthates first prepared by Schmidbaur,[14] and the heterobridged, ylide complex $Au_2[\mu\text{-}(CH_2)PPh_2][\mu\text{-}S_2COR]$ (R = Me, Et, Pr^i).[15] The structure of the related polymeric Ag(I) xanthate, $[Ag(^{n}Bu\text{-xanthate})]_n$, has been reported to contain eight-membered rings in a chair conformation. Parallel units are connected by bridging Ag−S bonds to form a two-dimensional network with an intramolecular Ag···Ag distance of 3.130 Å.[16]

In this paper, we describe the synthesis and characterization of two dinuclear gold(I) xanthate complexes, $[Au(\mu\text{-}S_2COR)]_2$ (R = Et, Bu^n). The structure of the *n*-Bu xanthate derivative reported here is the first presented for a binary Au(I) xanthate, although the related dithiocarbamate, 1,1-dithiolate, dithiophosphonate, and dithiophosphate and ylide complexes of gold(I) are well-known. The ethyl derivative unfortunately does not crystallize in a suitable fashion for a structure determination.

Experimental Section

General Methods. The potassium salt of ethyl xanthate was obtained commercially from ACROS Organics and recrystallized from dry ethanol before use. The potassium salt of the butyl xanthate was prepared according to reported procedures.[2a] Unless otherwise noted, all reactions and manipulations were carried out under an inert atmosphere with a positive nitrogen gas flow using standard Schlenk techniques. Methanol and ethanol were distilled from Mg turnings. Butanol (bp 117.7 °C) was distilled under N_2 atmosphere and oven dried over molecular sieves. Dichloromethane was distilled over P_4O_{10}. The tetrahydrothiophene and tetrabutylammonium hexafluorophosphate were used as purchased from Aldrich Chemical Co.

Instrumentation. Melting points were measured on a Unimelt capillary melting point apparatus and are reported uncorrected. ^1H NMR spectra were obtained on a Varian XL-200 spectrometer or a Varian UnityPlus-300 spectrometer. ^1H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in the deuterated solvent, and are reported as chemical shift position (δ_H), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), relative integral intensity, and assignment. Thermogravimetric studies were carried out with a DuPont TGA 951 instrument and TA Instruments TGA Q-500 at a heating rate of 10 °C/min under nitrogen. The resulting TGA residue of compound **2** was subjected to X-ray powder diffraction analysis.

Synthesis of Potassium Butyl Xanthate. Nitrogen is bubbled through a 50 mL portion of *n*-butyl alcohol (bp 117° C) in an oven-dried Schlenk flask. KOH (0.02 mol) is suspended in the alcohol with vigorous stirring. CS_2, 1.2 mL (0.02 mol), is added dropwise to the KOH saturated solution over a period of 30 min. After

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(5) (a) Fackler, J. P., Jr.; van Zyl, W. E.; Prihoda, B. A. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; John Wiley & Sons: West Sussex, England, 1999; p 795. (b) Mansour, M. A.; Connick, W. B.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *J. Am. Chem. Soc.* **1998**, *120*, 1329. (c) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (d) Daws, C. A.; Exstrom, C. L.; Sowa, J. R.; Mann, K. R. *Chem. Mater.* **1997**, *9*, 363. (e) Konugi, Y.; Mann, K. R.; Miller, L. L.; Exstrom, C. L. *J. Am. Chem. Soc.* **1998**, *120*, 589. (f) Yam, V. W.; Cheng, E. C. *Gold Bull.* **2001**, *34*, 20. (g) Yam, V. W.; Chan, C. L.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1996**, 4019. (h) Yam, V. W.; Li, C. K.; Chan, C. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 2857. (i) Yam, V. W.; Chan, C. L.; Li, C. K.; Wong, K. M. *Coord. Chem. Rev.* **2001**, *216*−*217*, 173.

(6) Lee, Y. A.; McGarrah, J. E.; Lachicotte, R. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2002**, *124*, 10662.

(7) van Zyl, W. E.; López-de-Luzuriga, J. M.; Mohamed, A. A.; Fackler, J. P., Jr.; Staples, R. *Inorg. Chem.* **2002**, *41*, 4579.

(8) Lawton, S. L.; Rohrbaugh, W. J.; Kokotailo, G. T. *Inorg. Chem.* **1972**, *11*, 2227.

(9) Maspero, A.; Kani, I.; Mohamed, A. A.; Omary, M. A.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **2003**, *42*, 5311.

(10) (a) Grohmann, A.; Schmidbaur, H. *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: London, 1995. (b) Schmidbaur, H.; Schier, A. *Science of Synthesis, Houben-Weyl*; Georg Thieme Verlag: Stuttgart, Germany, 2004; Vol.3. (c) Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 6959. (d) Laguna, A.; Laguna, M. *Coord. Chem. Rev.* **1999**, *193*−*195*, 837.

(11) Cavell, K. J.; Sceney, C. G.; Hill, J. O.; Magee, R. J. *Thermochim. Acta* **1973**, *5*, 319.

(12) Assefa, Z.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1994**, *33*, 2790.

(13) Paparizos, C.; Fackler, J. P., Jr. *Inorg. Chem.* **1980**, *19*, 2886.

(14) Bergfeld, M.; Schmidbaur, H. *Chem. Ber.* **1969**, *102*, 2408.

(15) Bardaji, M.; Jones, P. G.; Laguna, A.; Laguna, M. *Organometallics* **1995**, *14*, 1310.

(16) Xuhong, J.; Weiguang, Z.; Yun, Z.; Suelein, W. *Chem. J. Internet* **2002**, *4*, http://www.chemistrymag.org/cji/2002/04b053ne.html.

addition of about half of the CS_2, the solution becomes light yellow. After the addition of more than 0.65 mL of CS_2, the clear yellow solution turns cloudy. The cloudy yellow solution is then left to stir for 1 h, after which a yellow precipitate starts to form. After stirring of the mixture for an additional 1 h, filtration gives 0.78 g (79% yield) of product. The very light and fluffy precipitate is washed with *n*-butanol and put into the desiccator containing KOH and left overnight. The product turns from yellow to orange at 232 °C and decomposes completely at 250 °C to a black material. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.63 (t, O−CH_2), 1.81 (q, OCH_2CH_2), 1.48 (m, CH_3CH_2), 0.91 (t, CH_3).

Synthesis of Gold(I) Dimer of *n*-Butyl Xanthate, 1. A 52.0-mg amount (0.276 mmol) of recrystallized potassium butyl xanthate was dissolved in 30 mL of dry acetone, under nitrogen. The light yellow solution was cooled in an ice bath. and 85.3 mg (0.266 mmol) of Au(THT)Cl was dissolved in 5 mL of CH_2Cl_2 and added to the ligand solution. The mixture was stirred for 3 h during which a light green precipitate formed. The product was filtered off, washed twice with water, and dried under vacuum (55.4 mg, 70%) and recrystallized from CH_2Cl_2. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.55 (t, O−CH_2), 1.87 (q, OCH_2CH_2), 1.5 (m, CH_3CH_2), 1.00 (t, CH_3). Anal. Calcd for $C_{10}H_{18}Au_2O_2S_4$: H, 2.60; C, 17.34. Found: H, 2.48; C, 17.38. Solid-state IR spectroscopy of $[Au(\mu\text{-}S_2COBu^n)]_2$, **1**, shows a group of bands between 1056 and 1195 cm^{-1} assigned to ν_{C-O} and ν_{C-S} coupled modes. The K butyl xanthate shows similar bands at frequencies 1070 and 1149 cm^{-1}.

Synthesis of Gold(I) *n*-Ethyl Xanthate Dimer, 2. A 52.7-mg amount (0.329 mmol) of recrystallized potassium ethyl xanthate was dissolved in 30 mL of dried acetone under nitrogen. The light yellow solution was cooled in an ice bath, and 100.7 mg (0.314 mmol) of Au(THT)Cl was dissolved in 5 mL of CH_2Cl_2 and added to the ligand solution. The mixture was stirred for 3 h during which a light yellow precipitate was formed and filtered off. The product was washed twice with water and dried under vacuum (86.3 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.60 (q, O−CH_2), 1.53 (t, CH_3). Anal. Calcd for $C_6H_8Au_2O_2S_4$: C, 11.23; H, 1.45. Found: C, 11.49; H, 1.38. Solid-state IR spectroscopy of $[Au(\mu\text{-}S_2COEt)]_2$, **2**, shows a group of bands between 1042 and 1198 cm^{-1} assigned to ν_{C-O} and ν_{C-S} coupled modes. The K ethyl xanthate shows similar bands at frequencies 1045 and 1101 cm^{-1}.

Structure Determination. Data were collected using a Siemens (Bruker) SMART CCD (charge-coupled device) based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using cryogenic grease. Data were measured using ω scans of 0.3°/frame for 60 s, such that a hemisphere was collected. The first 50 frames were recollected at the end of data collection as a monitor for decay. No decay was detected. Cell parameters were retrieved using SMART[17] software and refined using SAINT[18] on all observed reflections. Data reductions were performed using SAINT software. Absorption corrections were applied using SADABS.[19] The structure was solved by direct methods using SHELXS-97[20] and refined by least squares on F^2, with SHELXL-97 incorporated in SHELXTL-PC V 5.03.[21]

Table 1. Crystallographic Parameters of **1**

empirical formula	$C_{10}H_{18}Au_2O_2S_4$
fw	692.46
temp	110(2) K
wavelength	0.710 73 Å
cryst system	orthorhombic
space group	$P2_12_12$
unit cell dimens	$a = 37.254(14)$ Å, $\alpha = 90°$ $b = 7.287(3)$ Å, $\beta = 90°$ $c = 6.054(2)$ Å, $\gamma = 90°$
V, Z	1643.4(11) Å^3, 4
density (calcd)	2.799 Mg/m^3
abs coeff	18.332 mm^{-1}
reflns collcd	8171
indep reflns	2792 ($R_{int} = 0.0955$)
data/restraints/params	2792/90/167
GOF on F^2	1.068
Flack param	0.0(2)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0706, wR2 = 0.1772

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1**

Bond Distances			
Au(1)−S(2)	2.274(7)	Au(2)−S(3)	2.289(7)
Au(1)−S(1)	2.291(7)	Au(2)−S(4)	2.312(7)
Au(1)−Au(2)	2.8494(15)	S(1)−C(6)	1.69(3)
O(1)−C(1)	1.30(3)	S(2)−C(1)	1.71(3)
O(1)−C(2)	1.47(3)		
Bond Angles			
S(2)−Au(1)−S(1)	173.2(2)	S(2)−Au(1)−Au(2)	94.44(16)
S(1)−Au(1)−Au(2)	92.30(18)	S(3)−Au(2)−S(4)	173.6(2)
S(3)−Au(2)−Au(1)	94.04(17)	S(4)−Au(2)−Au(1)	92.29(16)
S(4)−C(1)−S(2)	131.7(17)	S(1)−C(6)−S(3)	132.6(18)

The structure was determined in the space groups $P2_12_12$ by analysis of systematic absences. The Flack parameter indicates that the correct enantiomer is reported here. The carbon atoms of the butyl chains are disordered at C(4), C(5), C(9), and C(10). The largest positive difference peak and difference hole of 4.77 and 5.09 e·Å^{-3}, respectively, are at 0.96 and 1.48 Å from Au(2) and Au(1). The hydrogen atom positions were calculated by geometrical methods and refined as a riding model. The crystallographic details are given in Table 1. Selected bond distances and angles are presented in Table 2.

Luminescence Measurements. Emission and excitation spectra were recorded on a SLM AMINCO, model 8100, spectrofluorometer equipped with a xenon lamp. Spectra were corrected for instrumental response. Solid-state low-temperature measurements were made using a cryogenic sample holder of local design. Powder samples were attached to the holder with a mixture of copper powder, Cryogen oil (used for mounting crystals for X-ray structures) and collodion (a ether and alcohol soluble transparent nitrocellulose). The glue was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements with various slush baths for the other temperatures recorded. Although these xanthates have limited solubility in chloroform and dichloromethane solvents, **1** has sufficient solubility to produce a red emission upon UV excitation when the solution is frozen at 77 K. Visual observations of the luminescence in a few other solvents suggests that the solvent has little influence on the emission energy.

Electrochemical Measurements. Cyclic voltammetry experiments were conducted using a Bioanalytical Systems Inc. electrochemical analyzer, model 100, under computer control. CV measurements were performed in methylene chloride with 0.1 M Bu_4NPF_6 as supporting electrolyte. Fresh solutions containing 10

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(17) *SMART V 4.043 Software for the CCD Detector System*; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(18) *SAINT V 4.035 Software for the CCD Detector System*; Bruker Analytical X-ray Systems: Madison, WI, 1995. *SAINT V 4.035 Software for the CCD Detector System*; Bruker Analytical X-ray Systems: Madison, WI, 1995.

(19) SADABS. Program for absorption corrections using Siemens CCD based on the method of Robert Blessing. Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

(20) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

(21) *SHELXTL 5.03 (PC-Version), Program Library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems: Madison, WI, 1995.

mL of the supporting electrolyte were prepared prior to each CV experiment. Each solution was deoxygenated by purging with nitrogen for 2−5 min. Background CV's were acquired before the addition of the gold complexes. A three-electrode system was used, comprised of a platinum (1.6 mm diameter) working electrode, a platinum wire auxiliary electrode, and a silver/silver chloride (Ag/AgCl) reference electrode. The working electrode was wiped prior to each experiment with fine sand paper and rinsed. Potentials are reported vs Ag/AgCl at room temperature and are not corrected for junction potentials. Each CV experiment was repeated a number of times at different scan rates.

Results and Discussion

Synthesis and Characterization. Potassium alkyl xanthates are prepared by saturating the corresponding alcohol with potassium hydroxide and then adding carbon disulfide. The fluffy light yellow products are stable at room temperature and decompose at 232 °C (potassium butyl xanthate) and 215 °C (potassium ethyl xanthate). The compounds do not melt without change but rather turn from light yellow to orange approaching the melt temperature and then decompose to black products of unknown composition.

Complexes **1** and **2** are synthesized by the reaction of Au(THT)Cl, THT = tetrahydrothiophene, with K[^{n}Bu-xanthate] and K[Et-xanthate] (1:1 stoichiometric ratio) in acetone at 0 °C, giving a light green or yellow powder in ∼60% yield. The products are sparingly soluble in chloroform, dichloromethane, ethanol, chlorobenzene, and acetone and have a characteristic sulfur odor. The solubility of the complexes increases upon heating. Cooling a solution of **1** and **2** in acetone or ethanol results in precipitation of the complex. The resultant analytically pure complexes have been characterized by ^{1}H, elemental analysis, UV−vis, and IR spectroscopy. Mass spectroscopic studies by electrospray ionization (ESI) for complexes **1** and **2** yielded complicated fragmentation patterns. Molecular ions were not observed, instead only gold fragments consistent with the presence of $[Au(S_2COBu)_2]^-$ and $[Au_4(S_2COBu)_3]^+$.

An unstable melt is formed at 115 °C for **1** and 108 °C for **2**. Each turns from light green to black, at 135° for **1** and 120° for **2**. Thermal decomposition of xanthates in the solid state is known to form several products including dixanthogens, olefins, alcohols, elemental sulfur, dialkyl xanthates, mercaptanes, mercaptides, and metallic sulfides in addition to CS_2 and COS.[2a]

Thermal properties of the complexes of diethyldithiocarbamic acid, EtdtcH, with gold(III) have been reported using TGA techniques.[22] The decomposition of $Au(Et_2dtc)Cl_2$ and $Au(Et_2dtc)_3$ in a nitrogen atmosphere occurs with evidence of a double endothermic peak indicating that melting occurs along with the decomposition. For each complex studied, gold metal is formed at 255 °C. The thermogravimetric (TG) and differential thermal analysis (DTA) curves of the light green compound **2** in a nitrogen atmosphere exhibit a gradual mass loss starting at about ≥120 °C and reach a plateau corresponding to metallic gold at >180 °C. X-ray powder diffraction of the residue, collected after heating to >200 °C, shows the expected cubic powder diffraction pattern of metallic gold. In addition, there is a small quantity of elemental sulfur.

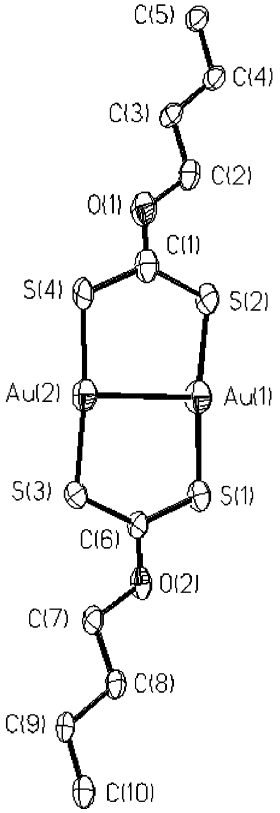

Figure 1. Structure of [Au_2(^{n}Bu-xanthate)$_2$], **1**, at 50% probability. Hydrogen atoms are omitted for clarity.

*Complex **1** was found to be very difficult to crystallize*. Numerous attempts, including slow diffusion of reactants into solution, were used in attempts to grow single crystals of **1** and **2**. Inevitably only powders were obtained in most organic solvents. A variety of different solvent combinations, such as ether−dichloromethane, hexane−dichloromethane, and pentane−dichloromethane were used. All solvent mixtures produced an oily product or film. Trials to grow crystals using the previous procedures at low temperature yielded thin plates of low X-ray quality crystals, and indexing was not successful. Crystal growth by very slow evaporation from a large volume of acetone (ca. 400 mL) over a few months successfully produced X-ray-quality crystals.

Structure. The structure of [Au_2(^{n}Bu-xanthate)$_2$] was determined by X-ray crystallography. A thermal ellipsoid drawing is shown in Figure 1, and selected bond distances and angles are listed in Table 2. Complex **1** crystallizes in the orthorhombic space group $P2_12_12$ with four molecules in the unit cell. The atoms in the eight-membered $Au_2S_4C_2$ ring are essentially in one plane. The average Au−S bond length is 2.27 Å, and the S−Au−S angle is 173.4°. The intramolecular Au(1)···Au(2) distance of 2.8494(15) Å is shorter than that observed in metallic gold (2.884 Å).[23] The closest Au···Au distance between two independent molecules

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[22] D'Ascenzo, G.; Bica, T. *Thermochim. Acta* **1977**, *18*, 301.

[23] Pearson, W. D. *Lattice Spacing and Structure of Metal and Alloys*; Pergamon Press: London, 1957.

Table 3. Dinuclear Gold(I)−Sulfur Compounds and Their Au···Au Distances and Solid-State Luminescence Spectral Data (nm)

complex	excitation	emission	Au···Au (Å)	ref
$[Au(^{n}Bu\text{-xanthate})]_2$	450	690	2.849	*a*
$[AuS_2PPh_2]_2$	380	451, 495	2.96, 3.09	26
$[AuS_2PPh(OEt)]_2$	400	453, 496	3.10, 3.12	28
$[AuS_2P(O^{i}Pr)_2]_2$	432	468, 524	3.05, 3.10, 2.91[b]	7
$[PPN]_2[Au(\mu^2\text{-}\eta^2\text{-}CS_3)]_2$			2.79	29
$[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$	388	495, 527	2.80	30
$[AuS_2CN(C_5H_{11})_2]_2$	460	630	2.76	5b

[a] This work. [b] Intermolecular distance.

in the unit cell is ~3.643 Å. The angle between the planes containing the molecules in the unit cell is ~69.56°. The hydrophobic butyl groups prevent short intermolecular interactions between the chains.

The S−C−S angle in **1**, ~132°, is larger than in potassium butyl xanthate,[24] ~123°, presumably due to the fact that this angle is in the bridge in **1**. Partial double-bond character is found in the S_2C−O linkages of **1**, C−O = 1.38 Å, but apparently less than in potassium butyl xanthate where this distance is 1.32 Å. While hindered rotation was observed[13] about the S_2C−O bond in Me_2AuS_2CO(2,6-dimethylphenyl), it was not observed for **1** with the solubility conditions available. The sum of the angles about the S_2C−O carbon atom is 359.97°, indicating that there is no significant deviation from planarity in the S_2CO group. The two butyl groups are anti to each other in the solid state and adopt their normal zigzag shape. The structural influence of the Au(I) atoms on the ligand π electron delocalization appears to be about the same as observed with Ni(II).[25]

The Au···Au distance, 2.85 Å, in **1** is shorter than the Au···Au distance found in the dinuclear dithiophosphinate $[AuS_2PPh_2]_2$ (3.09 Å),[26] ylide $[Au(CH_2)_2PPh_2]_2$ (2.97 Å),[27] and dithiophosphonate $[AuS_2PPh(OEt)]_2$ (3.10 Å)[28] complexes. However, this distance is longer than in the other 1,1-dithiolates structurally studied, $[PPN]_2[Au_2(\mu^2\text{-}\eta^2\text{-}CS_3)_2]$ (2.79 Å),[29] $[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$ (2.80 Å),[30] and $[AuS_2C{-}N(C_5H_{11})_2]_2$ (2.76 Å),[5b] Table 3. These latter dithiolates contribute a large π electron donation to the carbon (and sulfur) atoms of the ligands. While theoretical and experimental data exist relating the aurophilic distance to "softness" of the ligands,[31] recent calculations[32] suggest that other electronic factors may be involved such as ligand π donation, which can cause the HOMO to be δ^* rather than the ususal σ^*.[33]

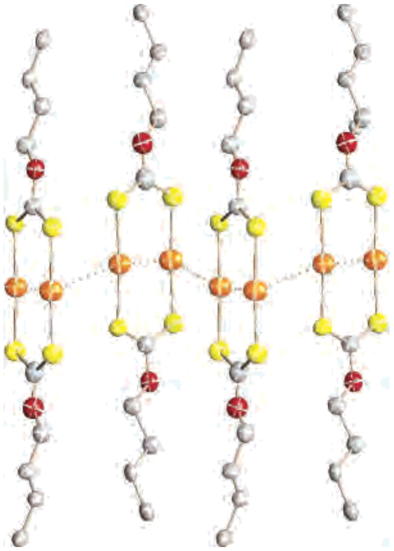

Figure 2. Packing diagram for **1**.

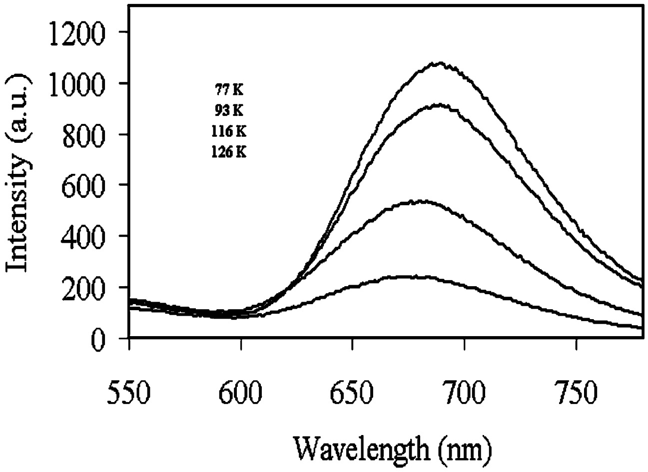

Figure 3. Emission spectrum of **1** in the solid state at four temperatures, with the 77 K spectrum being the most intense.

Luminescence. The absorption spectra of potassium butyl and ethyl xanthates in chloroform show a band of high intensity at ~308 nm, (ϵ = ~1.9×10^4 L M^{-1} cm^{-1}, π−π^*) and a band of low intensity at ~380 nm (ϵ = ~22 L M^{-1} cm^{-1}, n−π^*). Compared to the bands in the xanthate anion, the intense band at ~308 nm is blue shifted slightly to ~288 nm in the complexes; however, the band at ~380 nm is blue shifted significantly to ~328 nm in the gold complexes.

Compounds **1** and **2** are not photoluminescent at room temperature under UV light; however, they show a strong red luminescence that is easily visible to the eye at temperatures below 150 K in the solid state. Excitation at 450 nm gives an emission spectrum with a broad asymmetric profile, peaking near 690 nm and tailing to 850 nm (Figure 3). Complex **1** has a large Stokes shift ($\Delta\nu$ > 8500 cm^{-1}), which suggests considerable structural distortion from the ground state to the excited state. Complex **1** emits at a lower energy

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(24) Kashaev, A. A.; Liopo, V. A.; Leonov, S. B.; Kazakova, L. Z.; Frolova, N. A. *Kristallografiya* **1979**, *24*, 590.

(25) Coucouvanis, D.; Fackler, J. P., Jr. *Inorg. Chem.* **1967**, *6*, 2047.

(26) van Zyl, W. E.; López-de-Luzuriga, J. M.; Fackler, J. P., Jr.; Staples, R. *Can. J. Chem.* **2001**, *79*, 896.

(27) (a) King, C.; Wang, J.-C.; Khan, M. N. I.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 2145. (b) Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Tocher, J.; Mazany, A. M.; Trzcinska-Bancroft, B.; Knachel, H.; Dudis, D.; Delord, T. J.; Marler, D. O. *J. Am. Chem. Soc.* **1985**, *107*, 6908.

(28) (a) van Zyl, W. E.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem. Commun.* **1998**, *1*, 51. (b) van Zyl, W. E.; Lopez-de-Luzuriaga, J. M.; Fackler, J. P., Jr. *J. Mol. Struct.* **2000**, *516*, 99.

(29) Vicente, J.; Chicote, M.-T.; Herrero, G. P.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1995**, 745.

(30) Nazrul, Md.; Khan, I.; Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 3579.

(31) Pyykko, P. *Angew. Chem., Int Ed. Engl.* **1997**, *97*, 597.

(32) Perez, L. M. Private communication (to be published).

(33) Carlson, T. F.; Fackler, J. P., Jr. *J. Organomet. Chem.* **2000**, *596*, 237.

than $[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$ (λ_{em} = 495 and 527 nm, Au⋯Au = 2.80 Å)[30] or the ylide $[Au(CH_2)_2PPh_2]_2$ (λ_{em} = 483 nm, Au⋯Au = 2.97 Å).[27]

Luminescence studies of mononuclear gold(I) xanthate complexes such as $(Ph_3PAu)_2S_2COEt$ and $(CEPAu)_2S_2COR$ (CEP = tris(cyanoethyl)phosphine; R = Me, Et, Bu) generally show a broad asymmetric emission (ca. 490 nm) assigned as ligand-centered ($\pi-\pi^*$ transition) on the basis of the nature of the emission.[12] In these mononuclear gold(I) phosphine complexes, the Stokes shift is small and the absorption profile generally resembles the emission. By contrast, the emission of **1** presumably originates from LMCT with the intramolecular Au⋯Au interaction probably producing some LMMCT (LMMCT = ligand−metal−metal charge transfer).[5i] Au−Au bond formation in the excited state, an occurrence consistent with the large Stokes shift observed and the low energy of the emission, further suggests LMMCT may be important. Intermolecular LMMCT also could play some role on the basis of the 3.68 Å ground-state separation of dimers. The lack of spectral change in solution, however, does not support this.

It is seen in Table 3 that compounds with intramolecular Au−Au interactions about ∼3.1 Å show emission bands ranging from 400 to 500 nm such as for $[AuS_2PPh_2]_2$ (423 nm) and $[AuS_2PPh(OEt)]_2$ (319 and 417 nm).[26,28] Compound **1** has a shorter intramolecular Au−Au interaction (2.850 Å) compared with these compounds but displays a large red shift (680 nm). While the shift probably is influenced by the short Au−Au ground-state interaction, the emission energy is an excited-state phenomena and depends on other factors as well. The compound $[Au(S_2C{-}N(C_5H_{11})_2)]_2$ has a shorter Au(I)⋯Au(I) distance, 2.76 Å, than **1** but the emission is blue shifted to 630 nm.[5b] The electronic effect of the ligands on the excited-state energy of these dinuclear Au⋯Au compounds must play some role. Exciplex formation also cannot be excluded from consideration by the studies we have performed here, but if it does occur, it would arise from intermolecular Au⋯Au interactions between dinuclear units in the excited state. The solid-state structure (Figure 2) suggests that relatively little motion of the dinuclear units would be required to bring the gold atoms together in the excited state.

The possibility that one can predict the presence of weak intermolecular Au⋯Au ground-state interactions in dinuclear gold−sulfur complexes from their emission spectra was tested with the complex $[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$.[30] It shows no intermolecular Au−Au interaction but does show two emission bands (495, 527 nm) at 77 K (Table 3). Subsequent studies of the ligand itself showed that the yellow potassium salt luminesces at 77 K with an emission at 553 nm. Hence, the 527 nm emission of the complex, which has a similar emission profile, is attributed to the ligand. This phenomenon was not seen for any of the other complexes investigated. All had colorless, nonluminescent dithiolate ligands. Thus, it appears, for this series of complexes, that the emission profile can predict the presence of intermolecular Au−Au interactions (producing a low-energy LMMCT emission), provided that the ligand emission spectrum is known.

Attempts to oxidatively add chlorine to **1** and **2** using $PhI{\cdot}Cl_2$ at low temperature were unsuccessful and resulted in decomposition of the complexes. These results agree with observations for most other neutral dithiolates although Burmeister[34] did observe color changes upon oxidation of gold(I) dithiocarbamates which were suggestive of the formation of dinuclear gold(II) products. The $[n\text{-}Bu_4N]_2[AuS_2C{=}C(CN)_2]_2$ and the mixed-ligand dithiophosphinate ylide complexes[35] are the only dinuclear dithiolate Au(I) complexes which have produced Au(II) products sufficiently stable to be isolated and structurally characterized, although the former materials do rearrange in solution to gold(III) and gold(I) products. Accumulated data regarding the reactivity of dinuclear and polynuclear metal complexes are consistent with the ability of neighboring metal atoms and coordinated ligands to influence the oxidative addition process generally, both positively and negatively.[35] Cationic metal centers or electron-withdrawing ligands near the oxidation center can be expected to stabilize the HOMO or “closed-shell” ground state. This increases the HOMO−LUMO separation, thereby making oxidative addition less favorable. Electron-rich anionic complexes or complexes with strongly donating ligands will decrease the HOMO−LUMO separation rendering the oxidative addition process more feasible.

The electrochemical oxidation of the K butyl xanthate in 0.1 M Bu_4NPF_6/CH_2Cl_2 shows an irreversible peak at 0.42 V (sulfur-based oxidation) vs Ag/AgCl. The peak is assigned to the oxidation of the xanthate to form a S−S bond as $[SC(S)O^nBu]_2$.[2a] However, the electrochemical oxidation of **1** in 0.1 M Bu_4NPF_6/CH_2Cl_2 at 100 mV/s shows two irreversible oxidation peaks at 1.15 V (sulfur-based oxidation) and 1.55 V vs Ag/AgCl, typical of gold(I) thiolate oxidation investigated before.[36] The phosphine−Au(I) thiolate complexes [LL(Au-*p*-thiocresolate)$_2$], LL = disphosphine, undergo a broad irreversible oxidation at about +0.6 to +1.1 V and a second, sharper, irreversible oxidation at more positive potentials, +1.2 to +1.6 V (vs SCE). Electrochemical studies[37] show that the ylide $[Au(CH_2)_2PR_2]_2$ in 0.1 M Bu_4NBF_4/THF undergoes two quasi-reversible, stepwise (presumably one electron) oxidations at 0.11 and 0.23 V vs Ag/AgCl at scan rate of 100 mV/s. The situation, however, is complicated by the precipitation of a yellow material of unknown composition, in the immediate vicinity of the Pt working electrode.

Conclusions

As part of our ongoing studies of gold−sulfur compounds, we reported the chemistry derived from the reaction between

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(34) Calabro, D. C.; Harrison, B. A.; Palmer, G. T.; Moguel, M. K.; Rebbert, R. L.; Burmeister, J. L. *Inorg. Chem.* **1981**, *20*, 4311.

(35) Fackler, J. P., Jr. *Polyhedron* **1997**, *16*, 1−17.

(36) (a) Mohamed, A. A.; Chen, J.; Bruce, A. E.; Bruce, M. R. M.; Krause Bauer, J. A.; Hill, D. T. *Inorg. Chem.* **2003**, *32*, 2203. (b) Mohamed, A. A.; Bruce, M. R. M.; Bruce, A. E. *Met. Based Drugs* **1999**, *6*, 233. (c) Chen, J.; Jiang, T.; Wei, G.; Mohamed, A. A.; Homrighausen, C.; Krause Bauer, J. A.; Bruce, A. E.; Bruce, M. R. M. *J. Am. Chem. Soc.* **1999**, *121*, 9225.

(37) Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Tocher, J.; Mazany, A. M.; Trzcinska-Bancroft, B.; Knache1, H.; Dudis, D.; Delord, T. J.; Marler, D. O. *J. Am. Chem. Soc.* **1985**, *107*, 6908.

monoanionic, potentially bidentate xanthate sulfur ligands and gold(I) to yield dinuclear gold(I) xanthates. The structure of the dinuclear gold(I) butyl xanthate shows a Au•••Au interaction of 2.84 Å with weak intermolecular interaction. Gold(I) xanthate complexes emit in the red at ∼690 nm. The vapochromic behavior of related complexes observed by Eisenberg is not observed with xanthates. Thermal stability of gold xanthates shows that they decompose at low temperatures to yield mainly gold metal. The lack of stability and the difficulty obtaining xanthate products capable of being crystallographically characterized clearly makes these materials relatively less valuable for detailed studies of the type that have been done with other related gold(I) dithiolates.

Acknowledgment. The Robert A. Welch Foundation of Houston, TX, and the National Science Foundation REU program (for support of A.O.R.) are gratefully acknowledged for financial support of this work.

Supporting Information Available: An X-ray crystallographic information file (CIF) for dinuclear gold(I) butyl xanthate and UV−vis, TGA, and DTA plots. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0349858