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Article

Gold(I)−Dithioether Supramolecular Polymers: Synthesis, Characterization, and Luminescence

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A series of discrete compounds and supramolecular polymers were synthesized by self-assembly of dithioether building blocks and $HAuCl_4 \cdot 3H_2O$. In complexes **1** {[Au**L**$^{1\text{-}Me}$Cl], where **L**$^{1\text{-}Me}$ is bis(methylthio)methane} and **2** {[Au$_2$**L**$^{2\text{-}Ph}$Cl$_2$], where **L**$^{2\text{-}Ph}$ is 1,2-bis(phenylthio)ethane}, adjacent units are connected via aurophilic interactions. Complex **1**, a one-dimensional (1D) supramolecular polymer, and complex **2**, a two-dimensional supramolecular network, both feature nearly linear $[Au-Au-]_\infty$ chains. Complexes **4a**, **4b**, and **4c**, all of which contain 1,3-bis(phenylthio)propane (**L**$^{3\text{-}Ph}$), are polymorphs having the composition [Au$_2$**L**$^{3\text{-}Ph}$Cl$_2$]. Complex **3** {[Au$_2$**L**$^{1\text{-}Ph}$Cl$_2$], where **L**$^{1\text{-}Ph}$ is bis(phenylthio)methane}and complexes **4a** and **4b** consist of nearly identical 1D supramolecular polymers formed through Au−Au interactions. The third polymorph, **4c**, is a molecular complex, as it does not have metal−metal interactions. Complex **5** {[Au$_2$**L**$^{4\text{-}Ph}$Cl$_2$], where **L**$^{4\text{-}Ph}$ is 1,4-bis(phenylthio)butane} is also molecular. UV–vis spectra showed that the absorption bands of these complexes are allowed ligand-centered transitions between 230 and 260 nm. Complexes **1**, **2**, and **6** {[Au**L**$^{3\text{-}Me}$Cl], where **L**$^{3\text{-}Me}$ is 1,3-bis(methylthio)propane} exhibited solid-state luminescence at 5 K with vibronic progressions and band maxima at approximately 570 nm. It is suggested that complex **6** contains $[Au-Au-]_\infty$ chains.

Introduction

The synthesis and characterization of self-assembled supramolecular structures based on gold(I) building blocks is an active research area because of the interesting structural and spectroscopic properties of these materials.[1,2] Furthermore, self-assembly of metal−organic supramolecular polymers has attracted a great deal of attention because of the potential applications of these polymers as functional materials.[3–5]

We were interested in studying structured inorganic–organic frameworks built up by self-assembly of dithioether organic building blocks with Ag(I) and Au(I) in order to explore properties of metal−organic supramolecular compounds, such as anion exchange or luminescence. As dithioether building blocks (denoted **L**$^{n\text{-}R}$), we chose dithioethers **R**S(CH$_2$)$_n$S**R** having aliphatic chains between the sulfur atoms, where ***n*** is the number of CH$_2$ groups and **R** is an aryl or an alkyl group. These were combined with Ag(I) salts in order to form hybrid inorganic–organic supramolecular architectures.[6]

The selection of these ligands was motivated by four reasons: (1) according to the Pearson hard–soft acid–base

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concept,[7] silver(I) and gold(I) ions are soft Lewis acids and hence have good ability to coordinate to thioether ligands that are soft Lewis bases; (2) these symmetrical dithioether building blocks afford two coordination sites to d^{10} metal centers, expanding the coordination spheres of the metal centers into extended solid-state networks; (3) lengthening of the aliphatic segment between the S atoms increases the degree of conformation of these ligands,[8] allowing the effect of flexibility of the organic building blocks on the resulting coordination polymers to be studied; and (4) hindrance of the coordination spheres of the d^{10} metal centers may be affected by the bulk of the **R** substituent of the dithioether ligands. Thus, variation of the bulk of **R** allowed us to study its effect upon the topology of the resulting coordination polymers.

In supramolecular metal−organic frameworks obtained by the combination of these dithioether organic spacers and silver(I) salts, the Ag(I) coordination sphere was expanded by the dithioether ligands.[6] On the other hand, the aurophilic interaction between adjacent gold(I) atoms usually allows the expansion of Au(I) complexes into hybrid inorganic–organic extended solid-state networks.[2,9–13] This interaction has an energy on the order of 5–10 kcal mol^{-1} for a Au(I)−Au(I) distance of 3.05 Å, which is comparable to that of hydrogen bonds.[2,14] Individual Au(I)−Au(I) interactions may be considered weak. However, these weak interactions can cooperate in the solid state to form a stronger system, and as a result, many gold(I)−thioether complexes were found to be insoluble in common organic solvents.[14] Because of their insolubility, they could not be crystallized, making an accurate determination of the structures of those gold(I) coordination polymers difficult[14] and justifying the synthesis of soluble gold(I)−thioether compounds that can be crystallized in order to establish their structures.[14] To the best of our knowledge, there is only one gold(I)−$\mathbf{R}$S(CH$_2$)$_n$S$\mathbf{R}$ complex {[Au$_2$$\mathbf{L}^{2\text{-Ph}}Cl_2$], where $\mathbf{L}^{2\text{-Ph}}$ is 1,2-bis(phenylthio)ethane} whose structure has been characterized fully.[15] This structure was established at room temperature. One of our goals was to transpose our previous studies[6] of Ag(I)−$\mathbf{R}$S(CH$_2$)$_n$S$\mathbf{R}$ metal−organic frameworks (MOFs) to gold(I) by preparing and characterizing supramolecular gold(I)−$\mathbf{L}^{n\text{-R}}$ complexes. In addition, we were interested in the photoluminescence properties of such gold(I)−dithioether complexes.

Self-assembly of $\mathbf{L}^{n\text{-R}}$ dithioether molecules and gold halides may lead to the formation of a neutral molecular entity in which the sulfur atoms of $\mathbf{L}^{n\text{-R}}$ are coordinated to one or two gold(I) ions. In turn, these compounds may increase their dimensionalities via aurophilic interactions, as depicted in Chart 1.

Au(I)···Au(I) interactions and other structural features may be deduced from the interpretation of luminescence and Raman spectra.[16] In a recent report, Balch[17] has demonstrated the important influence of small structural variations on the electronic properties of gold(I) complexes. Furthermore, Fackler and co-workers[18] determined that the nature of the Au(I)−Au(I) interaction in the solid state has a profound influence on the optical properties of gold(I)−dithiophosphonate complexes. The electronic properties of these complexes strongly depend on the strength of the aurophilic interactions[18,19] and the number of Au(I)−Au(I) bonds.[16] Therefore, luminescence spectroscopy is now considered an important tool in the study of these compounds.

Here we report on the synthesis, structural characterization, and solid-state luminescence of several gold(I) complexes obtained by self-assembly of gold chloride with each of several dithioether building blocks. The organic building blocks used in this study were bis(methylthio)methane ($\mathbf{L}^{1\text{-Me}}$), bis(phenylthio)methane ($\mathbf{L}^{1\text{-Ph}}$), 1,2-bis(phenylthio)ethane ($\mathbf{L}^{2\text{-Ph}}$), 1,3-bis(phenylthio)propane ($\mathbf{L}^{3\text{-Ph}}$), 1,3-bis(methylthio)propane ($\mathbf{L}^{3\text{-Me}}$), and 1,4-bis(phenylthio)butane ($\mathbf{L}^{4\text{-Ph}}$).

Experimental Section

Materials and General Methods. Except for the ligands, all of the required reagents were commercially available and employed without further purification. Elemental analyses were performed by the Laboratoire d'analyse élémentaire (Université de Montréal). ^{1}H (300 MHz) NMR spectra in solution were recorded at 25 °C on a Bruker AV300; ^{1}H NMR chemical shifts (δ) are reported in parts per million and referenced to residual solvent signals of the deuterated solvents DMSO-d_6 ($\delta_{1\text{H}}$ = 2.50) and acetone-d_6 ($\delta_{1\text{H}}$ = 2.05). Luminescence spectra were recorded using a single-channel spectrometer, and the UV lines (333.6–363.8 nm) of an argon ion laser (Spectra-Physics Stabilite 2017) were used to excite crystalline samples inside a closed-cycle He cryostat (Sumitomo Heavy Industries SRDK-205). Luminescence was collected and dispersed using a 0.5 m monochromator (SPEX 500 M, 600 lines/mm) with a long-pass filter to remove the excitation (Schott KV-418) lines. Emitted light was detected using a photomultiplier tube (Hamamatsu R928) connected to a photon counter (Stanford Instruments SR 400). All spectra were corrected for instrument response using a tungsten lamp (Oriel 63350) according

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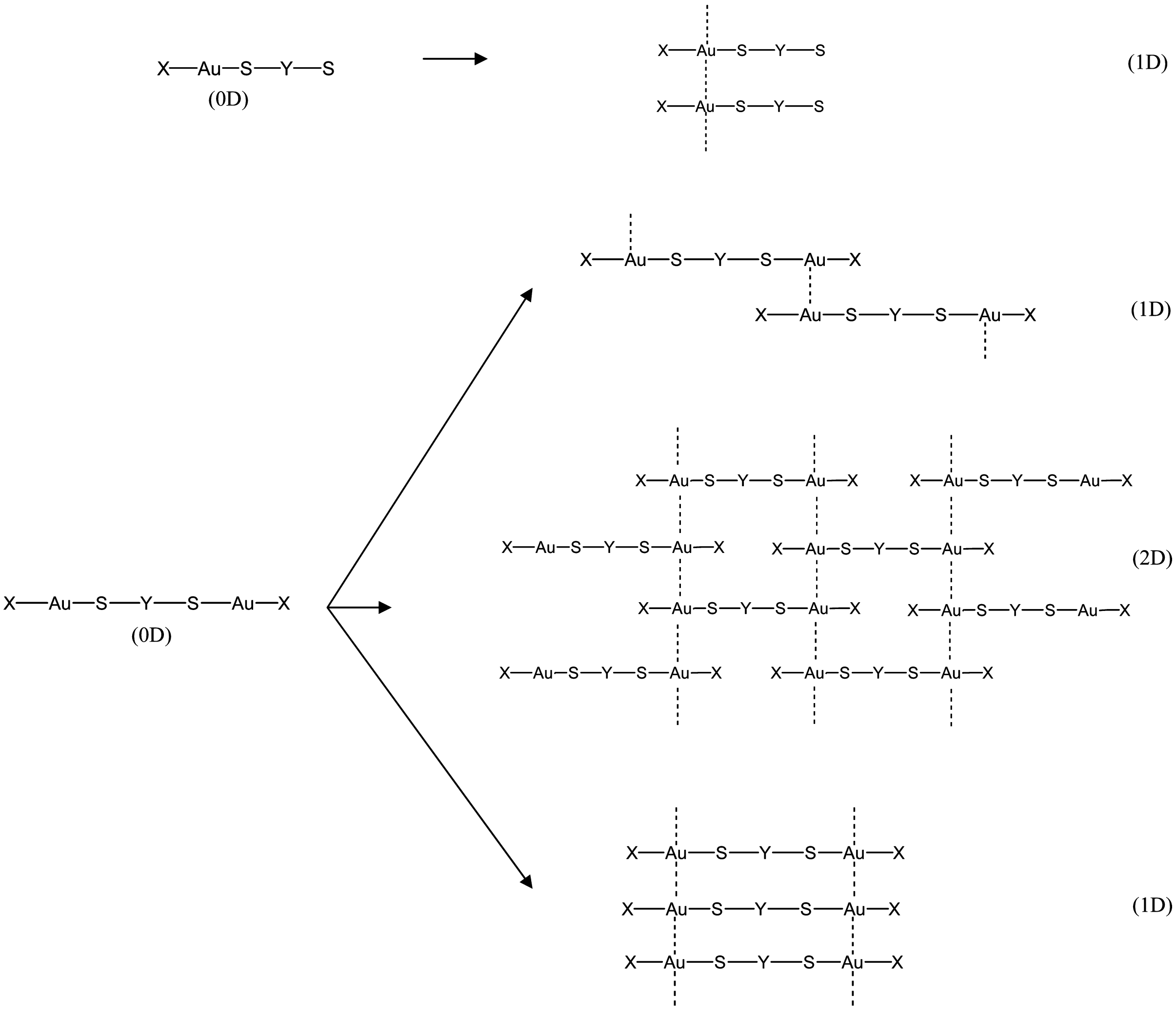
Chart 1. Discrete Molecules May Be Associated into One- or Two-Dimensional Networks via Aurophilic Interactions[a]



[a] X = Cl; Y = $(CH_2)_n$.

to a literature procedure.[20] Raman spectra were recorded with a Raman microscope (Renishaw System 3000). UV–vis spectroscopy was performed using a Cary 500i spectrometer.

Syntheses. The ligands ($\mathbf{L^{1\text{-}Me}}$, $\mathbf{L^{1\text{-}Ph}}$, $\mathbf{L^{2\text{-}Ph}}$, $\mathbf{L^{3\text{-}Ph}}$, $\mathbf{L^{3\text{-}Me}}$, and $\mathbf{L^{4\text{-}Ph}}$) were synthesized according to a published report,[21] and details of their characterization are provided in the Supporting Information.

$[AuL^{1\text{-}Me}Cl]_\infty$ (1). $HAuCl_4 \cdot 3H_2O$ (65 mg, 0.165 mmol) was dissolved in 10 mL of anhydrous ethanol at room temperature, forming a yellow solution. Upon the addition of $\mathbf{L^{1\text{-}Me}}$ (0.30 mL, 2.935 mmol), the solution first turned orange and then became colorless within 20 min. Hairlike crystals suitable for X-ray analysis grew from this solution within minutes. Yield: 90% based on $HAuCl_4 \cdot 3H_2O$. Anal. Calcd for $C_3H_8S_2AuCl$: C, 10.58; H, 2.37. Found: C, 10.09; H, 2.05. ^1H NMR (DMSO-d_6, 300 MHz): δ 2.089 (s, 6H, $\mathbf{CH_3}{-}S{-}CH_2{-}S{-}\mathbf{CH_3}$), 3.705 (s, 2H, $CH_3{-}S{-}\mathbf{CH_2}{-}S{-}CH_3$). Raman: ν(Au−S), 264.4 cm^{-1}; ν(Au−Cl), 387.6 cm^{-1}.

$[Au_2L^{2\text{-}Ph}Cl_2]_\infty$ (2). Dissolution of $HAuCl_4 \cdot 3H_2O$ (132 mg, 0.335 mmol) in 10 mL of anhydrous ethanol at room temperature yielded a yellow solution that turned orange upon the addition of $\mathbf{L^{2\text{-}Ph}}$ (150 mg, 0.608 mmol). Dropwise addition of diethyl ether (10 mL) over the course of 1 h caused the solution to change from orange to colorless. The solution was left to stand at room temperature. Colorless crystals suitable for X-ray analysis appeared after a few weeks. Yield: 79% based on $HAuCl_4 \cdot 3H_2O$. Anal. Calcd for $C_{14}H_{14}S_2Au_2Cl_2$: C, 23.64; H, 1.98. Found: C, 23.34; H, 2.11. ^1H NMR (DMSO-d_6, 300 MHz): δ 3.154 (s, 4H, $-S-(\mathbf{CH_2})_2-S-$), 7.218–7.431 (m, 10H, $C_6\mathbf{H_5}-$). Raman: ν(Au−S), 273.3 cm^{-1}; ν(Au−Cl), 375.3 cm^{-1}.

$[Au_2L^{1\text{-}Ph}Cl_2]_\infty$ (3). This complex was synthesized in the same manner as **2**, using $HAuCl_4 \cdot 3H_2O$ (128 mg, 0.325 mmol) and $\mathbf{L^{1\text{-}Ph}}$ (498 mg, 2.146 mmol). Colorless crystals were obtained after a few weeks. Yield: 54% based on $HAuCl_4 \cdot 3H_2O$. Anal. Calcd for $C_{13}H_{12}S_2Au_2Cl_2$: C, 22.40; H, 1.73. Found: C, 22.71; H, 1.77. ^1H NMR (DMSO-d_6, 300 MHz): δ 4.662 (s, 2H, $-S-\mathbf{CH_2}-S-$), 7.219–7.431 (m, 10H, $C_6\mathbf{H_5}-$). Raman: ν(Au−S), 257.7 cm^{-1}; ν(Au−Cl), 366.6 cm^{-1}.

$[Au_2L^{3\text{-}Ph}Cl_2]_\infty$ (4a). This complex was synthesized in the same manner as **2**, using $HAuCl_4 \cdot 3H_2O$ (133 mg, 0.338 mmol) and $\mathbf{L^{3\text{-}Ph}}$ (0.30 mL, 1.305 mmol). After about 3 weeks, crystals suitable for X-ray analysis were deposited. Yield: 76% based on $HAuCl_4 \cdot 3H_2O$. Anal. Calcd for $C_{15}H_{16}S_2Au_2Cl_2$: C, 24.84; H, 2.22. Found: C, 24.74; H, 2.36. ^1H NMR (DMSO-d_6, 300

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MHz): δ 1.846 (qt, 2H, −S−CH_2−$\mathbf{CH_2}$−CH_2−S−), 3.06 (t, 4H, −S−$\mathbf{CH_2}$−CH_2−$\mathbf{CH_2}$−S−), 7.145–7.328 (m, 10H, $C_6\mathbf{H}_5$−). Raman: ν(Au−S), 264.2 cm^{-1}; ν(Au−Cl), 341.7 cm^{-1}.

$[Au_2L^{3\text{-}Ph}Cl_2]_\infty$ (4b). $HAuCl_4\cdot3H_2O$ (121 mg, 0.307 mmol) was added to 10 mL of anhydrous ethanol, producing a yellow solution. Upon the addition of $\mathbf{L^{3\text{-}Ph}}$ (0.30 mL, 1.305 mmol), the solution turned orange. Dropwise addition of diethyl ether (10 mL) caused the solution to become colorless. This solution yielded crystals by diffusion into petroleum ether. After 2–3 weeks, colorless crystals suitable for X-ray analysis were deposited. Yield: 62% based on $HAuCl_4\cdot3H_2O$. Anal. Calcd for $C_{15}H_{16}S_2Au_2Cl_2$: C, 24.84; H, 2.22. Found: C, 24.61; H, 2.32. ^1H NMR (DMSO-d_6, 300 MHz): δ 1.853 (qt, 2H, −S−CH_2−$\mathbf{CH_2}$−CH_2−S−), 3.047 (t, 4H, −S−$\mathbf{CH_2}$−CH_2−$\mathbf{CH_2}$−S−), 7.135–7.323 (m, 10H, $C_6\mathbf{H}_5$−). Raman: ν(Au−S), 265.4 cm^{-1}; ν(Au−Cl), 344.1 cm^{-1}.

$[Au_2L^{3\text{-}Ph}Cl_2]$ (4c). This complex was synthesized as follows: $HAuCl_4\cdot3H_2O$ (135 mg, 0.343 mmol) was dissolved in 10 mL of anhydrous ethanol at room temperature. The yellow solution turned orange upon the addition of $\mathbf{L^{3\text{-}Ph}}$ (0.30 mL, 1.305 mmol). The solution was left to stand at room temperature for a few weeks, during which light-orange prismatic crystals suitable for X-ray analysis appeared. Yield: 68% based on $HAuCl_4\cdot3H_2O$. Anal. Calcd for $C_{15}H_{16}S_2Au_2Cl_2$: C, 24.84; H, 2.22. Found: C, 24.67; H, 2.24. ^1H NMR (DMSO-d_6, 300 MHz): δ 2.016 (qt, 2H, −S−CH_2−$\mathbf{CH_2}$−CH_2−S−), 3.093 (t, 4H, −S−$\mathbf{CH_2}$−CH_2−$\mathbf{CH_2}$−S−), 7.142–7.453 (m, 10H, $C_6\mathbf{H}_5$−). Raman: ν(Au−S), 266.3 cm^{-1}; ν(Au−Cl), 342.4 cm^{-1}.

$[Au_2L^{4\text{-}Ph}Cl_2]$ (5). The complex was synthesized in the same manner as **2**, using $HAuCl_4\cdot3H_2O$ (123 mg, 0.312 mmol) and $\mathbf{L^{4\text{-}Ph}}$ (209 mg, 0.761 mmol). After a few weeks, colorless crystals suitable for X-ray analysis were deposited. Yield: 85% based on $HAuCl_4\cdot3H_2O$. Anal. Calcd for $C_8H_9S_1Au_1Cl_1$: C, 25.99; H, 2.45. Found: C, 25.76; H, 2.24. ^1H NMR (acetone-d_6, 300 MHz): δ 1.823 (qt, 4H, −S−CH_2−($\mathbf{CH_2}$)$_2$−CH_2−S−), 3.025 (t, 4H, −S−$\mathbf{CH_2}$−(CH_2)$_2$−$\mathbf{CH_2}$−S−), 7.183−7.462 (m, 10H, $C_6\mathbf{H}_5$−). Raman: ν(Au−S), 262.2 cm^{-1}; ν(Au−Cl), 337.4 cm^{-1}.

$[AuL^{3\text{-}Me}Cl]$ (6). $HAuCl_4\cdot3H_2O$ (127 mg, 0.322 mmol) was added to 10 mL of anhydrous ethanol at room temperature, yielding a yellow mixture. Upon the addition of $\mathbf{L^{3\text{-}Me}}$ (0.30 mL, 1.305 mmol), an orange precipitate formed, and after a few minutes, a colorless microcrystalline powder was deposited. Yield: 82% based on $HAuCl_4\cdot3H_2O$. Anal. Calcd for $C_5H_{12}S_2AuCl$: C, 16.29; H, 3.28. Found: C, 16.34; H, 3.07. No NMR spectra were obtained for **6** because the complex could not be solubilized. Raman: ν(Au−S), 260.1 cm^{-1}; ν(Au−Cl), 370.1 cm^{-1}.

Structure Determination. X-ray intensity data for complexes **1** and **2** were obtained using a SMART 6K CCD instrument equipped with a rotating anode (Cu Kα, λ = 1.54178 Å) and a Mirror Montel 200 Optics monochromator. X-ray data for **3**, **4a**, **4b**, **5**, and **6** were obtained using a Brucker AXS Platform diffractometer equipped with a SMART 2K CCD area detector and graphite-monochromatized Cu Kα radiation. The program SAINT[22] was used for unit cell refinements and data reduction processing for **1**−**3**, **4b**, **5**, and **6**. An empirical absorption correction based on multiple measurements of equivalent reflections was applied using the program SADABS.[23]

Diffraction data for **4c** were collected on an Enraf-Nonius CAD-4 diffractometer using the ω-scan technique with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The unit cell dimensions were refined using CAD-4 software,[24] while NRC-2 and NRC-2A were used for data reduction.[25] An absorption correction based on the crystal geometry was applied.[25]

Space groups were confirmed using the XPREP[26] routine in the program SHELXTL.[27] The structures of **1**−**3** and **4a**−**4c** were solved using the Patterson method and difference Fourier techniques with SHELXS-97.[28] Refinements were performed on F^2 using full-matrix least-squares analysis. On the other hand, the structure of **5** was solved using direct methods and refined using full-matrix least-squares on F^2 with the SHELXTL program.[27] For complex **4b**, XPREP gave three possible space groups: *C*2, *Cm*, and *C*2/*m*. Since our starting materials were not chiral, we first tried to solve this structure in space groups *Cm* and *C*2/*m*, but neither gave a reasonable structure. On this basis, we finally solved **4b** in space group *C*2. The Flack parameter,[29] which had a value of 0.01(5) for **4b**, confirmed that the reported structure had the correct handedness. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions and included in the refinement using the riding-model approximation, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H) = 1.2U_{eq}(C)$ otherwise. A very small piece of **6** was mounted on a Smart 6K diffractometer equipped with a rotating anode (Cu Kα). Unfortunately, the data were not of sufficiently good quality, and the structure could not be solved. Crystal data, data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles for complexes **1**−**5** are listed in Table S1 in the Supporting Information.

Results

Synthesis of the Complexes. All of the syntheses started from Au(III) salts. These were reduced to the Au(I) oxidation state by the ligand, which was used in a slight excess. The reactions that took place are given in Chart S1 in the Supporting Information. The yellow solution of $HAuCl_4\cdot3H_2O$ in anhydrous ethanol turned to orange and then quickly changed to colorless as the ligand was added to the solution. The stoichiometry of the resulting complexes confirmed that gold was in the Au(I) oxidation state.

Al-Sa'ady et al.[30] reported that for the synthesis of gold(I)−thioether complexes, it was usually better to start from a gold(III) halide salt, allowing the thiodiglycol ligand to reduce gold(III) to gold(I). On the other hand, it has also been reported in the literature that spontaneous reduction of square planar Au(III) to linear Au(I) by various thiols is a favorable reaction.[31]

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Table 1. Crystal Data and X-ray Data Collection Parameters

	1	**2**	**3**	**4a**	**4b**	**4c**	**5**
formula	$C_3H_8S_2AuCl$	$C_{14}H_{14}S_2Au_2Cl_2$	$C_{6.5}H_6SAuCl$	$C_{15}H_{16}S_2Au_2Cl_2$	$C_{7.5}H_8SAuCl$	$C_{7.5}H_8SAuCl$	C_8H_9SAuCl
mol wt	340.63	711.21	348.60	725.23	362.615	362.615	369.63
crystal size (mm)	0.06 × 0.04 × 0.02	0.08 × 0.05 × 0.03	0.07 × 0.05 × 0.03	0.12 × 0.07 × 0.05	0.10 × 0.07 × 0.044	0.25 × 0.17 × 0.12	0.10 × 0.07 × 0.04
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
λ (Å)	1.54178	1.54178	1.54178	1.54178	1.54178	0.71073	1.54178
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$C2$	$C2/c$	$P2_1/c$
a (Å)	5.9972(2)	6.2629(2)	19.7419(4)	11.6093(3)	21.4504(6)	21.353(9)	11.9960(6)
b (Å)	20.3108(5)	8.9090(2)	10.5996(2)	8.5159(2)	5.6699(2)	10.049(7)	9.7548(5)
c (Å)	6.3029(1)	14.7547(4)	7.4895(2)	19.0202(5)	7.7774(2)	8.346(3)	8.5660(5)
α (deg)	90	93.667(1)	90	90	90	90	90
β (deg)	97.706(1)	92.614(1)	98.275(2)	102.788(2)	106.423(1)	91.04(3)	107.620(3)
γ (deg)	90	100.891(1)	90	90	90	90	90
V (Å^3)	760.81(3)	805.37(4)	1550.91(6)	1833.74(8)	907.31(5)	1790.6(1.6)	955.35(9)
Z	4	2	8	4	4	8	4
D_{calc} (g cm^{-3})	2.974	2.933	2.986	2.627	2.665	2.690	2.570
$F(000)$	616	644	1256	1320	660	1320	676
T (K)	150	100	200	220	220	100	220
μ (mm^{-1})	43.824	39.109	40.595	34.373	34.736	16.889	33.008
$\theta_{\max}$ (deg)	68.28	68.91	72.75	72.90	72.01	26.49	72.02
R^a [$I \geq 2\sigma(I)$]	0.0337	0.0618	0.0492	0.0419	0.1014	0.0363	0.0538
$R_w{}^b$ [$I \geq 2\sigma(I)$]	0.0885	0.1463	0.1234	0.0960	0.2372	0.0809	0.1338
R^a (all data)	0.0359	0.0707	0.0497	0.0460	0.1019	0.0747	0.0561
$R_w{}^b$ (all data)	0.0896	0.1567	0.1245	0.0982	0.2379	0.0843	0.1371
S^c	1.110	1.037	1.105	1.015	1.195	0.974	1.021

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2/(m - n)]^{1/2}$, where m is the number of reflections and n the number of parameters.

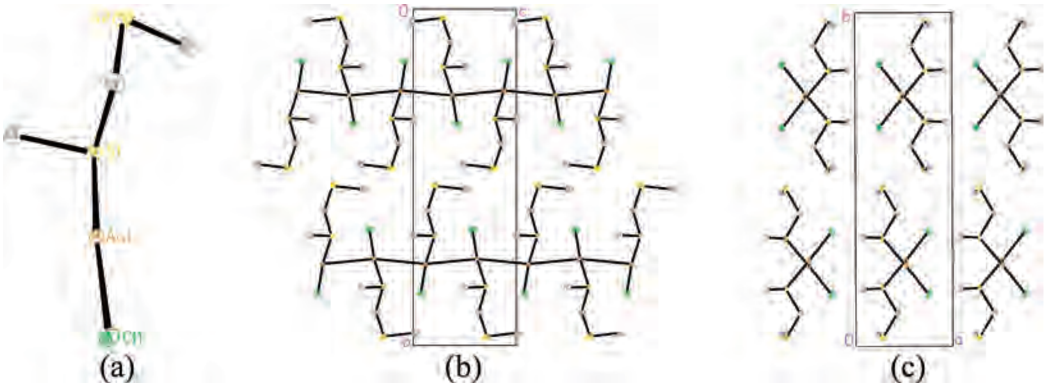

Figure 1. Complex **1**. (a) The chemical unit. (b) Side view of the chains in the unit cell. (c) Projection down the chain axis. Color code: C, gray; Cl, green; S, yellow; Au, orange. The hydrogen atoms are omitted for clarity.

Crystals of complexes **1** and **6** (containing $\mathbf{L}^{\mathbf{1\text{-}Me}}$ and $\mathbf{L}^{\mathbf{3\text{-}Me}}$, respectively) were formed within 20 min, while crystals of the other complexes suitable for crystal structure determinations were obtained after a few weeks.

When methanol or propanol was used instead of anhydrous ethanol to dissolve the gold salts, only complexes **1** and **6** were formed; the other complexes were not produced. Attempts to obtain complexes with different stoichiometries always failed, since the resulting complexes always had the same unit cell parameters regardless of the metal-to-ligand ratios of the starting materials. Except for **4c**, which was light orange, all of the crystalline complexes were colorless.

All of the complexes were soluble in common solvents except for **6**, which was found to be insoluble in any organic solvent. The metal-to-ligand ratio was 1:1 for both complexes in which **R** was a methyl group (**1** and **6**) and 2:1 for all of the other complexes (**2**−**5**), in which **R** was a phenyl group.

Out of 20 planned complexes, only eight provided material that could be used for crystal structure determination and/or luminescence studies. In many cases, the product we attempted to synthesize did not materialize, would not crystallize, or could not be recrystallized for lack of a suitable solvent. This was especially true when we attempted to study the influence of the anion. For example, none of the complexes containing bromide, nitrate, or acetate anions would crystallize. This inability to obtain crystals was attributed to the possibility of cooperative aurophilic interactions.[14]

Description of the Crystal Structures. A schematic description of the connectivities of the compounds reported here is shown in Chart S2 in the Supporting Information.

Complexes **1**, **3**, **4a**, and **4b** form one-dimensional (1D) supramolecular polymers, of which **3**, **4a**, and **4b** are topologically identical. Complex **2** is a two-dimensional (2D) supramolecular network. On the other hand, complexes **4c** and **5** are discrete molecules. When Au−Au interactions are taken into account in the description of the Au(I) coordination, the metal environment is square planar in **1** and **2**, T-shaped in **3**, **4a**, and **4b**, and linear in **4c** and **5**. Finally, the polymorphism observed for complexes **4a**−**4c** formed from self-assembly of $\mathbf{L}^{\mathbf{3\text{-}Ph}}$ and $HAuCl_4 \cdot 3H_2O$ is worth noting.

$[\mathbf{AuL}^{\mathbf{1\text{-}Me}}\mathbf{Cl}]_\infty$ (1). Self-assembly of the bis(methylthio)methane building block, $\mathbf{L}^{\mathbf{1\text{-}Me}}$, with the gold salt led to the formation of a 1D supramolecular polymer, $[\mathrm{Au}\mathbf{L}^{\mathbf{1\text{-}Me}}\mathrm{Cl}]_\infty$, having a metal-to-ligand ratio of 1:1 (Figure 1). The backbone of the polymer is an infinite chain of gold atoms.

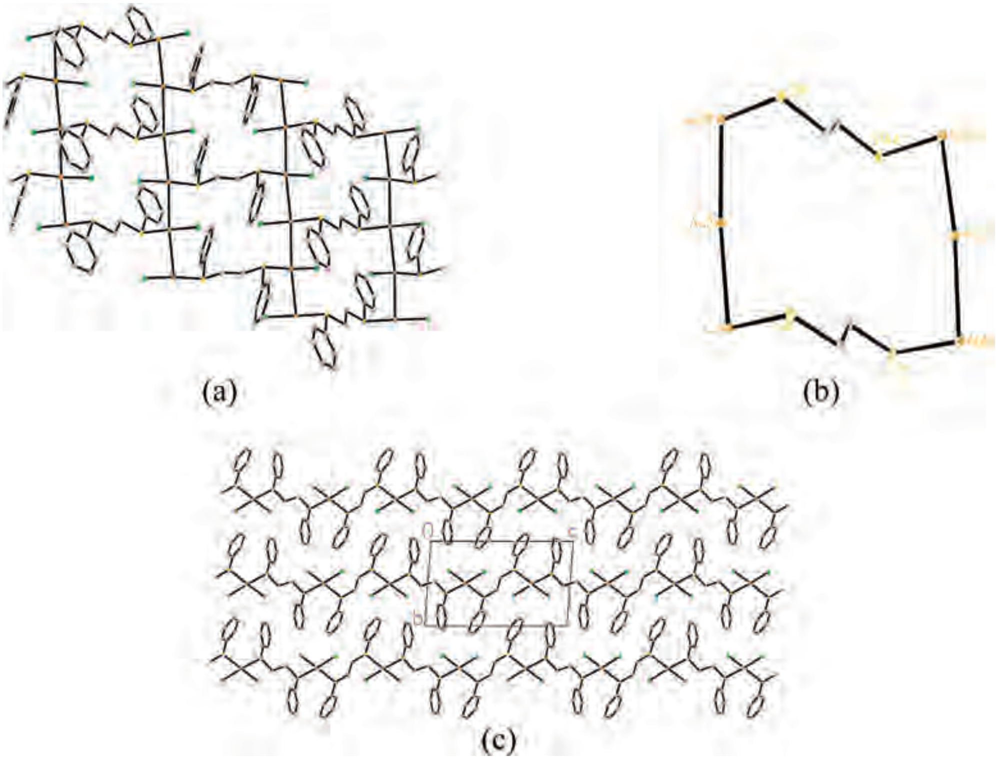

Figure 2. Complex **2**. (a) Projection showing $(Au-Au-)_\infty$ chains of **2** linked by the ligands, generating the 2D coordination network. (b) A Au_6L_2 macrocycle (the phenyl rings have been removed for clarity). (c) Side view of sheets of the 2D coordination network, parallel to the *ac* plane. Color code: C, gray; Cl, green; S, yellow; Au, orange.

A ligand molecule and a chlorine anion are coordinated to each gold atom. Each gold atom is surrounded by four neighbors (one Cl, one S, and two Au atoms) in a slightly distorted square planar coordination (Figure 1b and Figure S1a,b in the Supporting Information). In this complex, only one sulfur atom of the building block is coordinated to the gold center, while the second sulfur atom of the ligand and its methyl group lie between polymeric chains in layers parallel to the *ac* plane at intervals of *b*/2 (Figure 1b). The Au(I)−Au(I) distance between adjacent units is 3.1658(4) Å. This distance is in the normal range of 2.7690(7)–3.341(2) Å for aurophilic interactions,[32–40] indicating that some aurophilic interactions between adjacent $[Au\mathbf{L}^{1\text{-}Me}Cl]$ units exist. There are no interactions between the S atoms, since the S···S distance is 3.715 Å, which is larger than the sum of the van der Waals radii (3.60 Å)[41] for the sulfur atoms.

$[Au_2L^{2\text{-}Ph}Cl_2]_\infty$ (2). Complex **2** was obtained by the reaction of the 1,2-bis(phenylthio)ethane building block, $\mathbf{L}^{2\text{-}Ph}$, and the gold salt. Each ligand molecule is linked to two Au(I) metal centers to form a $[Au_2\mathbf{L}^{2\text{-}Ph}Cl_2]$ entity (Figure 2). Gold atoms of neighboring entities are linked to one another via aurophilic interactions, forming $[Au-Au-]_\infty$ infinite chains parallel to the *a* axis (Figure 2a). The resulting system is the 2D supramolecular network $[Au_2\mathbf{L}^{2\text{-}Ph}Cl_2]_\infty$. The Au(I)···Au(I) separations have values of 3.1204(5) and 3.1499(5) Å, which are in the normal range for aurophilic interactions.[32–40] The Au(I)−Au(I) chains are interlinked by ligand molecules, thus forming Au_6L_2 macrocycles (Figure 2b). In this complex, the two crystallographically independent Au(I) metal centers are surrounded by four neighbors in a slightly distorted square planar coordination (Figure S1c,d in the Supporting Information). As Drew and Riedl[15] established this structure from room temperature X-ray data, it is of interest to compare our results with theirs. The relative shrinkage of the unit cell volume, $\Delta V/V$, was −0.033 over a temperature interval of 173 °C. This effect was unevenly spread over the three crystallographic directions. In the *b* and *c* directions, $\Delta b/b$and $\Delta c/c$ were only −0.007 and −0.008, respectively. It was not surprising to observe that the most prominent shrinkage took place along the *a* direction, with $\Delta a/a = -0.026$, as the $[Au-Au-]_\infty$ chains lie in this direction. Because of the shrinkage of the unit cell, the Au−Au distances at 100 K [3.1204(5) and 3.1499(5) Å] were significantly shorter

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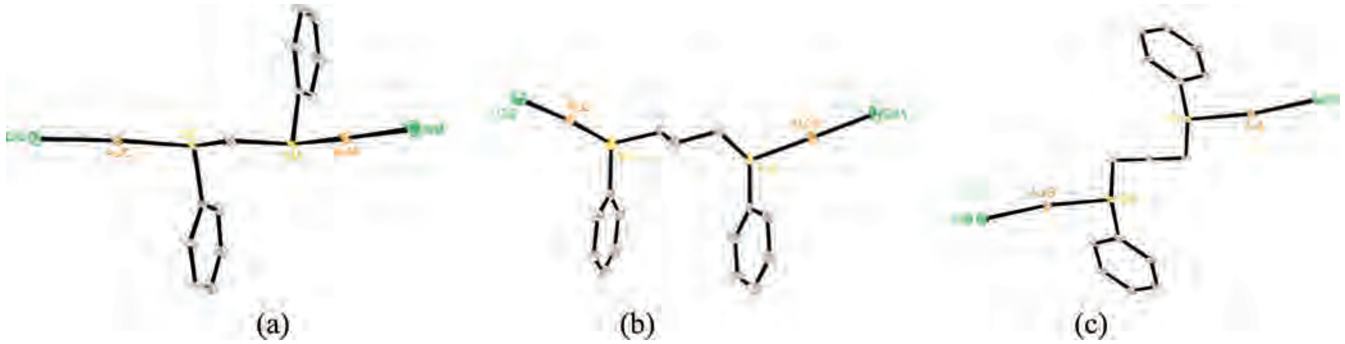

Figure 3. Comparison of the chemical repeat units in (a) complex **3**, (b) complex **4a**, and (c) complex **4b**.

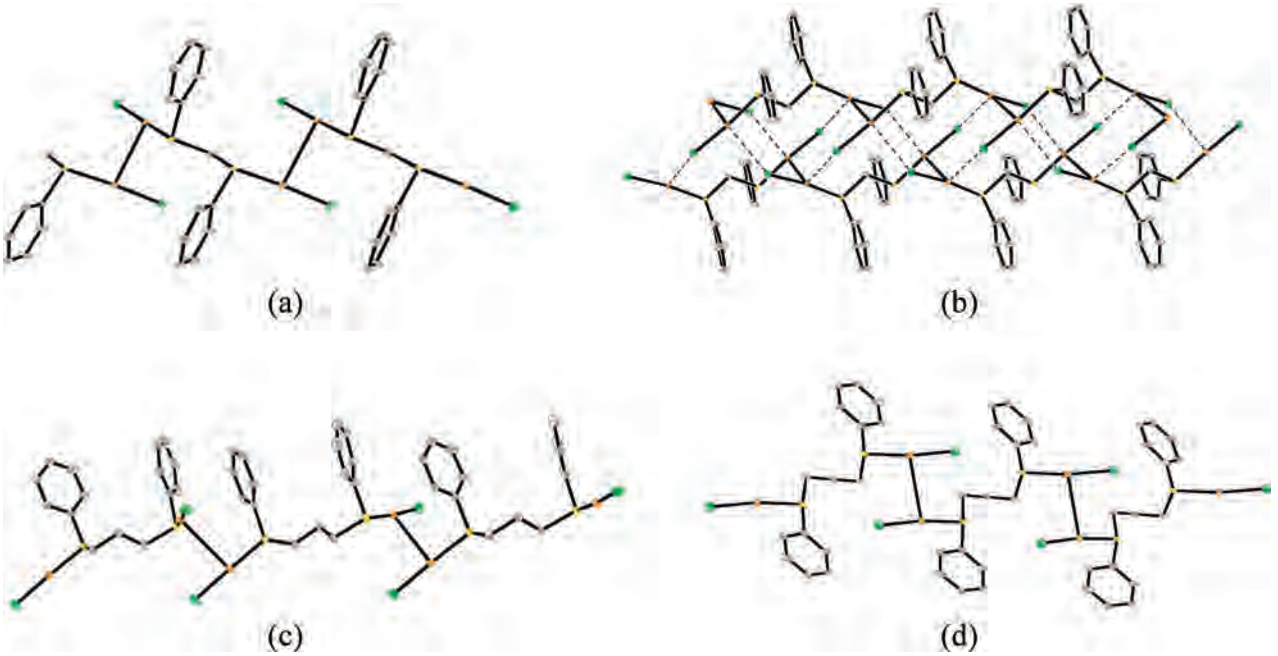

Figure 4. 1D coordination polymer chains in **3**, **4a**, and **4b**. (a) The single chain of **3**. (b) Formation of a double chain in **3** through weak Au···Cl interactions. (c) The single chain in **4a**. (d) The single chain in **4b**. Color code: C, gray; Cl, green; S, yellow; Au, orange.

than the corresponding quantities obtained at room temperature [3.187(2) and 3.209(2) Å] with relative $\Delta d/d$ values of −0.021 and −0.018, respectively.

$[Au_2L^{1\text{-}Ph}Cl_2]_\infty$ (3) and $[Au_2L^{3\text{-}Ph}Cl_2]_\infty$ (4a and 4b). Complexes **3**, **4a**, and **4b** have the same metal-to-ligand stoichiometry (2:1) and adopt very similar structures. Each gold atom has two neighbors (one S and one Cl), as shown in Figure 3a−c. A third neighbor, a gold atom, links the Au(Cl)−L−Au(Cl) molecule to another through aurophilic interactions, forming 1D supramolecular polymers in which the chemical repeat unit is [Au(Cl)−L−Au(Cl)−]. These linear chains are illustrated in Figure 4a,c,d. The Au−Au distances of 3.0347(4), 3.2997(4), and 3.1918(9) Å for **3**, **4a**, and **4b**, respectively, fall in the normal range indicating Au−Au aurophilic interactions, 2.7690(7)−3.341(2) Å.[32–40]

Complex **3** has weak Au−Cl interactions between neighboring polymer chains, since the Au−Cl distance [3.284(1) Å] is shorter than the sum of the Au and Cl van der Waals radii (3.41 Å).[41] Thus, this complex may best be described as a columnar supramolecular polymer (Figures 4b and 5d). Such secondary interactions were observed in the self-assembly of a gold salt with dimethylglyoxime, where the Au−Cl separation was 3.323(4) Å.[42] According to Simonov et al.[42] and Allen et al.,[43] 17 gold complexes listed in the Cambridge Structural Database (CSD) exhibit weak Au···Cl interactions characterized by a separation of 3.281−3.526 Å. It should be pointed out that since this interaction was observed only in **3**, it may be associated with the size of the ligand: $\mathbf{L^{1\text{-}Ph}}$ is the shortest ligand, which presumably allows for a closer approach of the chains.

The ligand torsion angles in **3**, **4a**, and **4b** (Figure 3a−c and Table 2) differ significantly from one another. The packing of the chains in these complexes is shown by projections on their *ab* or *ac* planes (Figure 5a–c).

Molecular Complexes $[Au_2L^{3\text{-}Ph}Cl_2]$ (4c) and $[Au_2L^{4\text{-}Ph}Cl_2]$ (5). Complexes **4c** and **5** were obtained by the combination of gold(I) with $\mathbf{L^{3\text{-}Ph}}$ and $\mathbf{L^{4\text{-}Ph}}$, respectively. The distances between Au atoms in adjacent $[Au_2\mathbf{L^{3\text{-}Ph}}Cl_2]$ components in complex **4c** and neighboring $[Au_2\mathbf{L^{4\text{-}Ph}}Cl_2]$ molecules in **5** (3.615 and 4.555 Å, respectively) are greater than 3.32 Å, which is twice the van der Waals radius of Au,[41] indicating that aurophilic interactions are absent in these complexes. In both **4c** and **5**, the gold atoms have a linear coordination (Figure 6a,b). Projections of the molecular

Table 2. Torsion Angles of Interest (deg) for the Complexes

	4a	**4b**	**4c**
Au−S−C−C	−173.7(1)	−170.5(1)	−176.2(1)
S−C−C−C	67.5(1)	−51.2(1)	−178.9(1)
C−C−C−S	178.4(1)	−51.2(1)	−178.9(1)
C−C−S−Au	−49.5(1)	−170.5(1)	−176.2(1)
	1		**2**
Au−Au−Au−Au	180	Au−S−C−C	−179.0(1)
		S−C−C−S	180
		Au−Au−Au−Au	180
	3		**5**
Au−S−C−S	178.9(1)	Au−S−C−C	176.5(1)
S−C−S−Au	178.9(1)	S−C−C−C	175.6(1)
		C−C−C−C	180

packing on the *ac* plane (Figure 7a,b) show the respective dispositions of the molecules in crystals of these complexes.

Discussion

Structural Aspects. One can see the effect of the bulk of the **R** substituent on the stoichiometry by comparing the structures of complexes **1** and **3** (Figures 1a and 3a). Indeed, for **R** = Ph (i.e., for complex **3** with ligand $\mathbf{L}^{\mathbf{1\text{-}Ph}}$), the two sulfur atoms of the ligand are coordinated to two different gold centers to form a $[\mathrm{Au_2}\mathbf{L}^{\mathbf{1\text{-}Ph}}\mathrm{Cl_2}]$ unit, while for **R** = Me (i.e., for complex **1** with ligand $\mathbf{L}^{\mathbf{1\text{-}Me}}$), only one sulfur atom of the ligand is bonded to a metal center to give $[\mathrm{Au}\mathbf{L}^{\mathbf{1\text{-}Me}}\mathrm{Cl}]$. In fact, all of the complexes involving phenyl-substituted ligands (**R** = Ph) contain the $[\mathrm{Au_2}\mathbf{L}^{\boldsymbol{n}\text{-}\mathbf{Ph}}\mathrm{Cl_2}]$ unit and have a metal-to-ligand ratio of 2:1, regardless of the aliphatic chain length in the ligand (***n*** = 1, 2, 3, or 4) . In contrast, the ligands containing the less-bulky methyl group [in complexes **1** and **6** (***n*** = 1 and 3, respectively)] seem to favor the $[\mathrm{Au}\,\mathbf{L}^{\boldsymbol{n}\text{-}\mathbf{Me}}\mathrm{Cl}]$ stoichiometry and a metal-to-ligand ratio of 1:1. A steric effect thus seems to control the stoichiometry of the resulting complexes.

The compounds synthesized here may be grouped into three different classes on the basis of the presence or absence and the type of aurophilic interactions:

Class 1. Complexes **1**, **2**, and possibly **6** (see Luminescence, below) possess cooperative aurophilic interactions. That is, their structures are based on the presence of infinite chains of gold atoms (Figures 1b and 2a).

Self-assembly of $\mathbf{L}^{\mathbf{3\text{-}Me}}$ and gold chloride led to the formation of complex **6**, which has a metal-to-ligand ratio of 1:1. However, good single crystals were not available for the determination of its structure.[44] The existence of a single gold atom per molecule of **1** allows for linear $[\mathrm{Au{-}Au{-}}]_\infty$ chains through aurophilic interactions. Hence, the structure is that of a 1D supramolecular polymer. On the other hand, because of its stoichiometry, each molecule of **2** is involved in two sets of aurophilic interactions, resulting in a 2D supramolecular polymer. The structure of **2** may be seen as consisting of adjacent $[\mathrm{Au{-}Au{-}}]_\infty$ chains linked by $\mathbf{L}^{\mathbf{2\text{-}Ph}}$ ligands.

Class 2. Complex **3**, containing the ligand $\mathbf{L}^{\mathbf{1\text{-}Ph}}$, and complexes **4a** and **4b**, containing the ligand $\mathbf{L}^{\mathbf{3\text{-}Ph}}$, belong to this group. Each gold atom is bound to only one other gold atom. Since a given chemical unit, $[\mathrm{Au_2}\mathbf{L}^{\mathbf{1\text{-}Ph}}\mathrm{Cl_2}]$ or $[\mathrm{Au_2}\mathbf{L}^{\mathbf{3\text{-}Ph}}\mathrm{Cl_2}]$, possesses two gold atoms, each unit is connected to two others via aurophilic interactions, generating topologically comparable 1D supramolecular polymers (Figure 4).

Class 3. The absence of short Au···Au contacts between adjacent $[\mathrm{Au_2}\mathbf{L}^{\mathbf{3\text{-}Ph}}\mathrm{Cl_2}]$ units in **4c** and $[\mathrm{Au_2}\mathbf{L}^{\mathbf{4\text{-}Ph}}\mathrm{Cl_2}]$ units in **5** results in molecular structures. It is suggested that Au···Au interactions are absent in these complexes because the aliphatic segments within the ligands are parallel to one another and the phenyl groups are disposed in opposite directions. Furthermore, the lengths of the aliphatic chains in these complexes are such that the Au atoms of neighboring molecules cannot face one another (Figure 7a,b).

The $\mathbf{L}^{\mathbf{4\text{-}Ph}}$ ligand in complex **5** and the $\mathbf{L}^{\mathbf{2\text{-}Ph}}$ ligand in complex **2**, which have an even number of $\mathrm{CH_2}$ groups in the aliphatic chain, are in the fully extended conformation (Table 2). This situation is common for symmetry-related molecules having an even number of methylene groups in their aliphatic chains. For example, the free ligands $\mathbf{L}^{\mathbf{2\text{-}Ph}}$, $\mathbf{L}^{\mathbf{4\text{-}Ph}}$, $\mathbf{L}^{\mathbf{6\text{-}Ph}}$, $\mathbf{L}^{\mathbf{8\text{-}Ph}}$, and $\mathbf{L}^{\mathbf{10\text{-}Ph}}$, each of which contains a crystallographic center of symmetry at the midpoint of its central $\mathrm{CH_2{-}CH_2}$ bond, all adopt the all-trans conformation.[8]

Polymorphism was observed in complexes containing the 1,3-bis(phenylthio)propane ligand, $\mathbf{L}^{\mathbf{3\text{-}Ph}}$. The three polymorphs **4a**−**4c** have identical $[\mathrm{Au_2}\mathbf{L}^{\mathbf{3\text{-}Ph}}\mathrm{Cl_2}]$ chemical units. Nevertheless, they have distinct Au···Au separations. Complexes **4a** and **4b**, in which the Au(I)−Au(I) distances are 3.2997(4) and 3.1918(9) Å, respectively, form 1D supramolecular polymers, while **4c**, with a Au(I)···Au (I) separation of 3.615 Å, is composed of discrete molecules (Figures 4 and 6). As shown by the torsion angles in the Au−S(Ph)−$(\mathrm{CH_2})_3$−S(Ph)−Au segment (Table 2), the polymorphs adopt clearly different conformations. In **4a** and **4b**, the phenyl groups of a given $\mathbf{L}^{\mathbf{3\text{-}Ph}}$ ligand lie on the same side of the aliphatic chain, while in **4c**, the phenyl groups are located on opposite sides of the aliphatic chain (Figures 3b,c and 6a). Complex **4a** has a trans−gauche−trans−gauche conformation, while the conformations of **4c** and **4b** are all-trans and trans−gauche−gauche−trans, respectively. Consequently, the dispositions of these three complexes in the solid state differ from one another (Figures 5b,c and 7a).

Although one is a molecule and the other a 1D supramolecular polymer, complex **4c** containing $\mathbf{L}^{\mathbf{3\text{-}Ph}}$ and complex **3** containing $\mathbf{L}^{\mathbf{1\text{-}Ph}}$ adopt very similar packing modes, as shown by their *ab*-plane projections (Figure S2 in the Supporting Information).

UV–Vis Spectroscopy. Electronic absorption data for complexes **1**−**5** in $\mathrm{CH_3CN}$ are listed in Table 3. Since complex **6** was insoluble in common organic solvents, its absorption spectrum could not be reported. All of the complexes displayed moderately intense absorption bands in the 234–256 nm range. The UV–vis spectra of the complexes were similar to those of the corresponding free ligands (as shown in Figures S3–S7 in the Supporting Information), and the main absorption bands of the com-

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[44] Crystal data for complex **6**: formula, $\mathrm{C_{25}H_{60}S_{10}Au_5Cl_5}$; fw = 1843.58; space group, $P2_1/c$; $a = 23.774(3)$ Å; $b = 9.244(1)$ Å; $c = 11.851(1)$ Å; $\beta = 119.415(5)°$; $V = 2268.55$ Å^3; $Z = 2$; $D_{\mathrm{calc}} = 2.699$ g cm^{-3}.

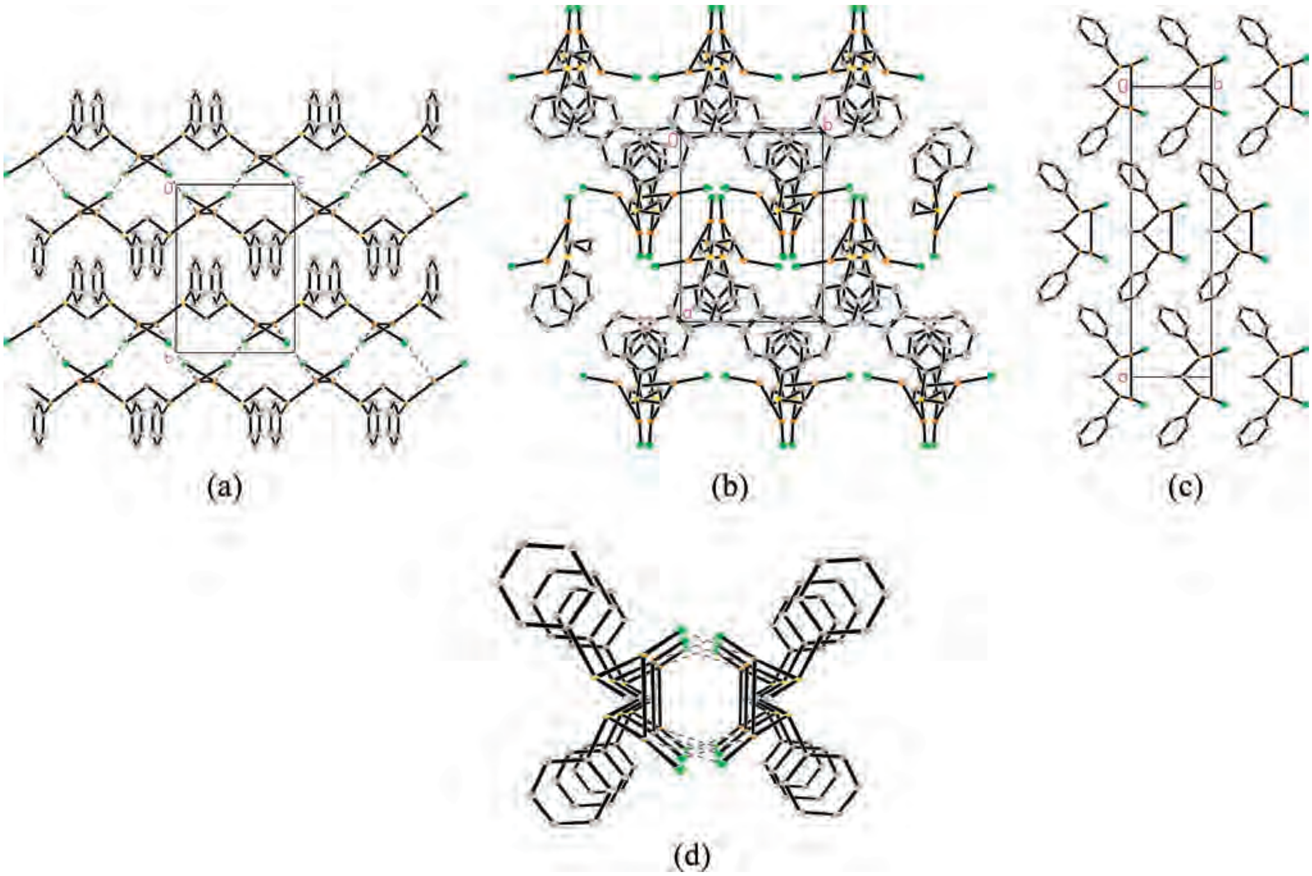
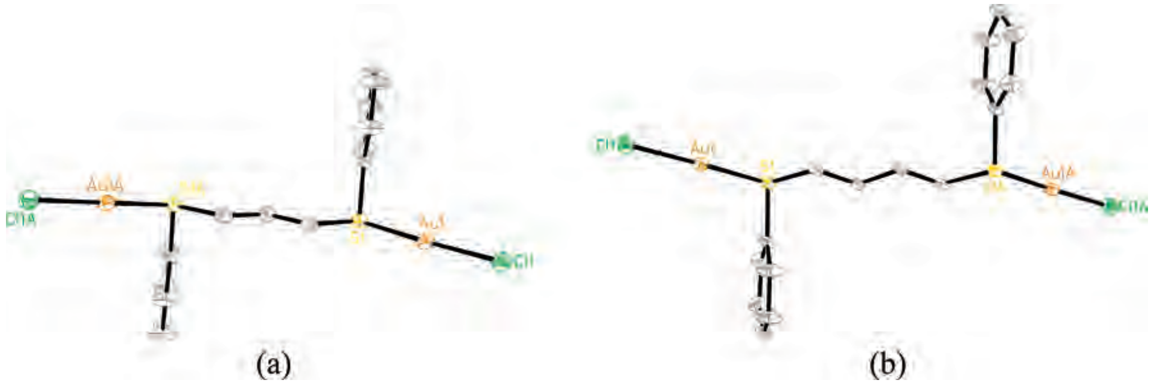

(a) (b) (c) (d)

Figure 5. Packing in complexes **3**, **4a**, and **4b**. (a) Projection of **3** along the *a* axis. Dotted lines indicate Au···Cl interactions. (b) Projection of **4a** along the *c* axis. (c) Projection of **4b** along the *c* axis. (d) Channel formation in **3**, as seen in a projection down the *c* axis. Color code: C, gray; Cl, green; S, yellow; Au, orange.



(a) (b)

Figure 6. Molecular complexes (a) **4c** and (b) **5**, both shown in the fully extended conformation. Color code: C, gray; Cl, green; S, yellow; Au, orange.

plexes could therefore be assigned to ligand-centered transitions.

Luminescence. To the best of our knowledge, no luminescence spectra with somewhat resolved vibronic structures (long progressions) have been reported for gold(I)−thioether complexes.

Solid-state emission spectra for complexes **1**, **2**, and **6** at 5 K are shown in Figure 8, and their characteristics are compared in Table 4. Luminescence energies and spectroscopic characteristics for many Au(I) compounds have been observed and shown to vary widely, from the ultraviolet to the orange spectral regions.[45] Luminescence intensities decrease with increasing temperature, and the compounds do not emit at room temperature. The emitting compounds **1** and **2** (which include ligands $\mathbf{L^{1\text{-}Me}}$ and $\mathbf{L^{2\text{-}Ph}}$, respectively) contain 1D-polymeric chains. Many different interpretations of the luminescence of gold(I) compounds have been proposed, including ligand-centered (LC),[46] metal-to-ligand charge-transfer (MLCT),[47] ligand-to-metal charge-transfer (LMCT),[39] metal-centered (MC),[48] or a combination of these categories.[49] Ab initio calculations (MP2 and CIS) on gold(I) cationic dimers containing thioether ligands[50] assigned the

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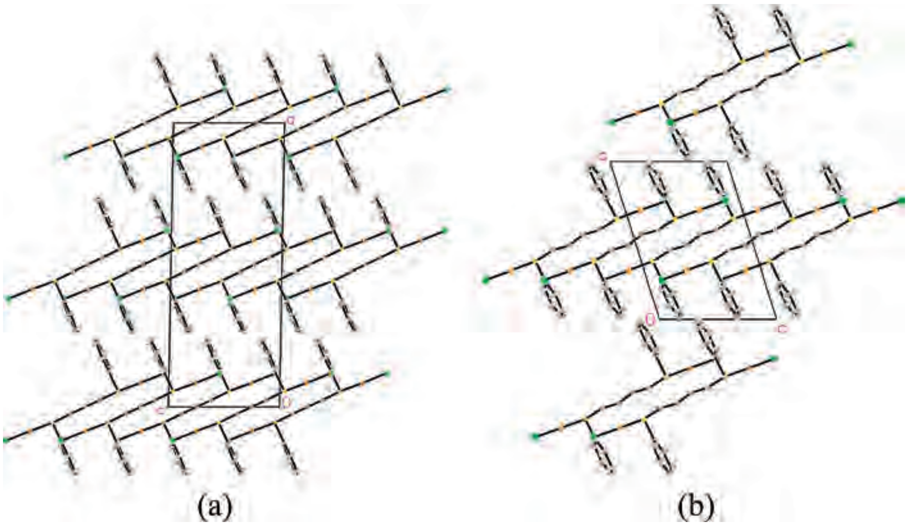

Figure 7. Projections showing the packing of (a) **4c** and (b) **5**. Color code: C, gray; Cl, green; S, yellow; Au, orange.

Table 3. Values of λ_{max} and ϵ for Complexes **1**−**5**

	1	**2**	**3**	**4a**	**4b**	**4c**	**5**
λ_{max} (nm)	234	255	256	254	255	256	254
ϵ (dm^3 mol^{-1} cm^{-1})	10216	12072	15276	14308	14588	15783	13018

luminescence to a predominantly metal-centered transition that also involved other excited states with similar energies. Metal-centered transitions are expected to shift to lower energies as the Au(I)−Au(I) distances decrease.[51] In contrast, the luminescence band maximum (E_{max}) for complex **2** (17900 cm^{-1}) was slightly higher in energy than that of **1** (17250 cm^{-1}), even though the Au–Au distance in **2** is shorter. The assignment from the computational study therefore cannot be applied to the compounds in the present work. Recent spectroscopic studies on molecular Au(I) thiolate phosphine mixed-ligand complexes with two and three Au(I) centers[52,53] have led to an assignment of the lowest-energy transition as a thiolate-to-Au(I) charge-transfer transition. The luminescence maxima of the literature complexes were located at wavenumbers on the order of 19000 cm^{-1}, a value which is somewhat greater than those observed for our complexes. The luminescence bands of some of these model complexes exhibited width at half-height ($W_{1/2}$) values comparable to those of the title compounds as well as barely resolved vibronic structure involving modes in the 400−800 cm^{-1} range that also resembled structure displayed by our complexes. These comparisons indicate that an LMCT assignment[52,53] appears reasonable.

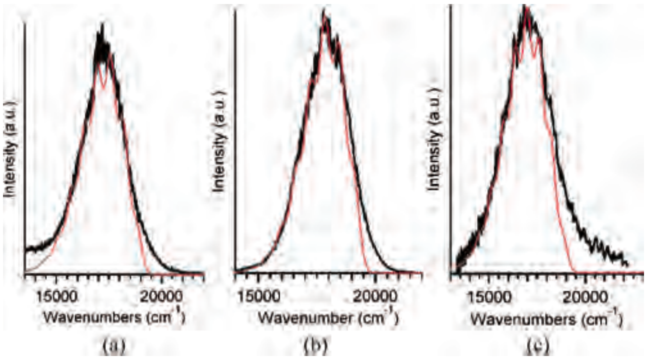

Figure 8. Solid-state luminescence spectra of (a) complex **1**, (b) complex **2**, and (c) complex **6** (black lines are experimental spectra, and red lines are luminescence fits).

Table 4. Luminescence Parameters for Complexes **1**, **2**, and **6**

	1	**2**	**6**
E_{max} (cm^{-1})	17250	17900	17000
$W_{1/2}$ (cm^{-1})	2400	2300	2800

The luminescence spectra of the compounds exhibited vibronic progressions (shoulders), as shown in Figure 8. The average progression interval was on the order of 600 cm^{-1}, indicating that emitting-state distortions occurred along normal coordinates other than the low-frequency metal−metal modes, leading to the large luminescence bands. Metal-centered luminescence has been reported for gold(I) compounds with sulfur ligands (dithiocarbonates), with spectra characterized by band widths of 1000 cm^{-1}.[19] Thus, those bands were narrower than the luminescence bands reported here (Table 4) by a factor of at least 2. The assignment as a purely metal-centered transition is therefore too simplistic, as the vibrational progressions revealed a contribution from the ligands (Figures S8 and S9 in the Supporting Information). Luminescence spectra can be calculated,[52,54] and such calculations gave satisfactory agreement with the experimental spectra in the present case, as illustrated in Figure 8. The calculated spectra were obtained with electronic origins set to 18950 and 19300 cm^{-1}, vibrational frequencies of 610 and 610 cm^{-1}, and dimensionless excited-state distortions

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of 2.22 and 2.52 for complexes **1** and **2**, respectively. The differing values obtained for the excited-state distortion reveal small but significant differences in the characteristics of the emitting states in the two complexes and quantitatively demonstrate the influence of differences in ligand structure on solid-state luminescence properties. The experimental luminescence spectrum of complex **6** was similar to those of **1** and **2** (Figure 8c). The spectrum was calculated with the electronic origin set at 18800 cm^{-1}, a vibrational frequency of 610 cm^{-1}, and a dimensionless excited-state distortion of 2.75. Although its crystal structure could not be established, we propose that complex **6** contains $[\mathrm{Au-Au-}]_\infty$ chains similar to those in **1** and **2** (Table 4), on the basis of the fact that these three complexes produced nearly identical luminscence spectra. Despite the highly sensitive instrumentation used, the luminescence of compounds **3**–**5** was too weak to be measured, even at the lowest temperatures.[55]

Concluding Remarks

In this study, we investigated the coordination chemistry of Au(I) complexes with dithioether ligands of the form $\mathbf{R}\mathrm{S(CH_2)}_{\mathbf{n}}\mathrm{S}\mathbf{R}$, containing a short aliphatic segment ($\boldsymbol{n} = 1-4$) and having $\mathbf{R}$ = methyl or phenyl. The metal-to-ligand ratios are 1:1 and 2:1 in complexes containing ligands with $\mathbf{R}$ = methyl and phenyl, respectively. The Au(I) coordination is T-shaped in **1** and **2** and linear in all of the other complexes. If Au–Au interactions are considered, the Au(I) coordination is square planar in **1** and **2** and T-shaped in the others.

The chemical repeat units in complexes **1**–**3**, **4a**, and **4b** are linked to one another via aurophilic interactions, giving rise to 1D and 2D supramolecular compounds, while **4c** and **5** are molecular complexes. The Au–Au distances in **1**–**3** and **4b** are 3.0347(4)–3.1918(5) Å and 3.2997(4) Å in **4a**. The polymeric compounds **1** and **2**, which contain Au(I) chains, $[\mathrm{Au-Au-}]_\infty$, exhibited solid-state luminescence with vibronic progressions at 5 K. The luminescence spectrum of **6** led us to conclude that this complex also contains $[\mathrm{Au-Au-}]_\infty$ chains. Polymorphism was observed for complexes **4a**–**4c** formed using 1,3-bis(phenylthio)propane as the dithioether ligand.

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Supporting Information Available: X-ray crystallographic information files in CIF format for compounds **1**–**5**, details of the characterization of the ligands, a table of bond distances and angles, and Figures S1–S9. This material is available free of charge via the Internet at http://pubs.acs.org.

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