Self-Assembly of Gold(I) Compounds with (Aza-15-crown-5)dithiocarbamate and 2-Mercapto-4-methyl-5-thiazoleacetic Acid

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ABSTRACT: Treatment of $AuCl(SMe_2)$ with equimolar sodium (aza-15-crown-5)dithiocarbamate (O_4NCS_2) or 2-mercapto-4-methyl-5-thiazoleacetic acid (HSSCOOH) in the presence of NaOMe affords a dinuclear complex, [Au-$(O_4NCS_2)]_2$ **1**, and a tetranuclear complex, $[Au(SSCOOH)]_4$ **2**, respectively. **1** features a dinuclear structure containing two azacrown ether rings, and there is a short intramolecular gold(I)···gold(I) distance of 2.7820(5) Å. Importantly, **2** crystallizes in two forms: **2**·4THF and **2**·4DMF, where the solvent molecules are hydrogen-bonded to the carboxylic acid moiety of SSCOOH. **2**·4THF and **2**·4DMF are tetranuclear complexes featuring an interesting double-clipped structure built from both thiazole rings and carboxylic acid moieties. The four gold(I) centers in **2** form a pucker-squared channel with four equivalent gold(I)···gold(I) distances of 3.0478(4) Å for **2**·4THF and 3.0423(4) Å for **2**·4DMF, respectively, and this one-dimensional channel structure may be rationalized by π···π interactions and/or weak intermolecular Au···S interactions of 3.800 Å for **2**·4THF or 3.986 Å for **2**·4DMF, respectively. Interestingly, with the same synthetic strategy **1** and **2** are formed with different nuclearities. This dramatic different structural motif between **1** and **2** may be ascribed to crystal packing of azacrown ether rings in part. At room temperature, **2** shows low-energy dual emissions with maxima at 585 and 720 nm, whereas it shows only a strong emission with a maximum at 585 nm at 77 K. This interesting luminescence property is suggested to be closely related to aurophilic interactions.

Introduction

The propensity for closed-shell d^{10} gold(I) centers to form weakly bonding interactions, leading to a large variety of supramolecular gold(I) compounds with novel structural and intriguing spectroscopic properties, has recently been an interesting and common feature in gold chemistry.[1–10] These interactions are typically identified by means of X-ray diffraction studies in all cases in which gold(I)···gold(I) distances are less than or close to the sum of the van der Waals radii (3.32 Å).[11] Mingos and co-workers[7a] used the reaction of $[Au(NH_3)_2]BF_4$ with *t*-BuC≡CH to synthesize the first gold(I)-containing catenane, [Au(*t*-BuC≡C)]₆, which was shown by X-ray diffraction to have close intra- and inter-ring gold-(I)···gold(I) contacts in a range between 3.2 and 3.5 Å. Puddephatt et al.[5a] have recently further elaborated the useful application of aurophilicity in the construction of supramolecular gold(I)-containing rings and catenanes by a self-assembly process.

The presence of aurophilic contacts may be recognized not only from short gold(I)···gold(I) distances and novel structural features, but also intriguing electronic absorption and luminescence properties. It is becoming clear that the gold(I)···gold(I) bonding interactions are responsible for the relevant transitions, and luminescence has thus become an important diagnostic tool for aurophilicity.[12] Recently, a spectacular experiment carried out by Balch et al.[3a] has demonstrated that luminescence of gold(I) complexes can be triggered by the solvation of the donor-free solid substrate either from the vapor phase or by dissolving the material in a solvent. In the meantime, a remarkable example of the strong solvent dependence of the luminescence of a gold-(I) compound in solution has also been observed by Che and co-workers.[10d] Moreover, an unusual chromic luminescence behavior linked to a structural change in the solid-state induced by exposure to the vapor phase of volatile organic compounds (VOCs) was also observed by Eisenberg and co-workers.[13] This "luminescent switch" for the detection of VOCs using gold(I) dimers, following the pioneering work by Mann and co-workers[14] on absorption and emission spectra of vapochromic platinum(II) and palladium(II) compounds, suggests that such gold(I) compounds hold great potential for analytical/sensor applications.

Zanazzi el al[15] in 1980 reported the first air-stable dithiocarboxylic acid derivative of gold(I), [Au(CH₃-CSS)]₄. In the tetranuclear structure, the four gold(I) centers are at the vertices of a rhomboid. The four bridging ligands are alternately above and below the plane of four gold(I) centers, where the molecule is almost symmetric and has an approximate D_2 symmetry. Another interesting example was reported by Jones et al.[16] in 1999, i.e., [Au(etu-H)]₄ (etu = imidazolidine-2-thione), in which the tetranuclear complex is further linked into chains by intermolecular gold(I)···gold(I) contacts. Thus, the interesting family of tetranuclear complexes [AuL]₄ (L = anionic ligands) seem still rare. However, molecular materials composed of discrete metal clusters are useful model systems for understand-

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Table 1. Crystallographic Data for 1, 2·4THF, and 2·4DMF

	1	**2·4THF**	**2·4DMF**
emp form	$C_{22}H_{40}Au_2N_2O_8S_4$	$C_{20}H_{28}Au_2N_2O_6S_4$	$C_{18}H_{26}Au_2N_4O_6S_4$
form wt	982.73	914.62	916.60
cryst sys	triclinic	tetragonal	tetragonal
space group	$P\bar{1}$	I_1/a	I_1/a
a (Å)	8.1657(2)	14.2833(6)	14.3972(9)
b (Å)	8.6329(2)	14.2833(6)	14.3972(9)
c (Å)	11.2093(3)	25.1256(11)	26.008(3)
α (°)	75.0558(10)	90	90
β (°)	85.0939(11)	90	90
γ (°)	88.4651(15)	90	90
V (Å^3)	760.65(3)	5125.9(4)	5390.9(8)
ρ_{calc} (g cm^{-3})	2.145	2.370	2.259
Z	1	8	8
μ (Mo−Kα) (cm^{-1})	99.53	118.00	112.23
F(000)	472	3456	3456
T (K)	150(1)	150(1)	273(2)
obsd reflns ($F_o \geq 2\sigma F_o$)	3501	2950	2112
refined parameters	173	132	137
R^a	0.0427	0.0319	0.0360
$R_w{}^b$	0.1013	0.0759	0.0833

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

ing surface chemistry and catalysis, but the synthesis of such materials is usually serendipitous. To date, gold-(I) thiolates are important substrates relevant to quite a number of applications from surface technology to drug design[2f] and virtually all of the classical and modern drugs based on gold(I) compounds for arthritis and rheumatism have been gold(I)-sulfur compounds.[17−19] In this context, we report here studies on self-assembly of gold(I) compounds with (aza-15-crown-5)dithiocarbamate and 2-mercapto-4-methyl-5-thiazoleacetic acid leading to the formation of dinuclear and tetranuclear complexes, respectively, in which the latter not only features a novel structural motif, but also shows interesting photoluminescence.

Experimental Section

General Information. All reactions were performed under a nitrogen atmosphere and solvents for syntheses (analytical grade) were used without further purification. NMR: Bruker DPX 400 MHz NMR; deuterated solvents with the usual standards. 2-Mercapto-4-methyl-5-thiazoleacetic acid (HSS-COOH) is commercially available, and sodium (aza-15-crown-5)dithiocarbamate (NaO$_4$NCS$_2$) was prepared by literature methods.[20]

Synthesis. [Au(O$_4$NCS$_2$)]$_2$ **1**: The reaction of NaO$_4$NCS$_2$ (318 mg) with AuCl(SMe$_2$) (295 mg) in CH$_2$Cl$_2$/MeOH (1:1, 50 mL) at room temperature for 4 h gave a pale yellow precipitate. The precipitate was filtered off in a vacuum, and **1** was obtained as a pale yellow solid in a 88% yield. Single crystals of **1** were grown by ether diffusion into a CH$_2$Cl$_2$/MeOH solution of **1**. ^{1}H NMR (DMSO-d_6, 25 °C): δ 3.699 [m, 12H, 6 -CH$_2$], 3.926 [t, 4H, J_{HH} 8.4 Hz, 2 -NCH$_2$CH_2], 4.071 [t, 4H, J_{HH} 8.7 Hz, 2 -NCH$_2$]. Anal. Calcd (%) for C$_{22}$H$_{40}$Au$_2$N$_2$O$_8$S$_4$: C, 26.89; H, 4.10; N, 2.85. Found (%): C, 26.86; H, 3.85; N, 3.01.

[Au(SSCOOH)]$_4$ **2**: The reaction of NaSSCOOH [211 mg, obtained from HSSCOOH (189 mg) and NaOMe (56 mg) in MeOH (25 mL)] with AuCl(SMe$_2$) (295 mg) in CH$_2$Cl$_2$/MeOH (1:1, 50 mL) at room temperature for 4 h gave a pale-yellow precipitate. The precipitate was filtered off in a vacuum and **2** was obtained as a pale yellow solid in a 95% yield. Single crystals of **2·4THF** were grown by slow evaporation of a THF solution and **2·4DMF** grown from ether diffusion into a DMF solution. Both solvated solvents are easily lost leading to crystal cracking. ^{1}H NMR (DMSO-d_6, 25 °C) δ 2.50 [s, 3H,

-CH$_3$], 3.68 [s, 2H, -CH$_2$-], 9.68 [s, 1H, -COOH]. Anal. Calcd (%) for C$_{24}$H$_{24}$Au$_4$N$_4$O$_8$S$_8$: C, 18.71; H, 1.57; N, 3.64. Found (%): C, 18.86; H, 1.75; N, 3.31.

Physical Measurements and Instrumentation. Steady-state emission spectra were measured on a SPEX Fluorolog-2 spectrophotometer, and emission lifetimes were measured with a Quanta Ray DCR-3 Nd:YAG laser (pulse output 355 nm, 8ns). The decay signal was recorded by a R928 PMT (Hamamatsu), connected to a Tektronix 2430 digital oscilloscope.

X-ray Crystallography. Suitable crystals were mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation (0.71073 Å) at 293 K for **2·4DMF** and 150 K for **1** and **2·4THF**. A preliminary orientation matrix and unit cell parameters were determined from three runs of 15 frames each, each frame corresponding to 0.3° scan in 15 s, followed by spot integration and least-squares refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART[21] software and refined with SAINT[22] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SAD-ABS.[23] The structure was solved by direct methods with the SHELX93[24] program and refined by full-matrix least-squares methods on F^2 with SHEXLTL-PC V 5.03.[24] All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Detailed data collection and refinement of the complexes are summarized in Table 1.

Results and Discussion

Complexes **1** and **2** were prepared by treating AuCl-(SMe$_2$) with equimolar NaO$_4$NCS$_2$ and NaSSCOOH, respectively (Scheme 1). Interestingly, with the same synthetic strategy complexes **1** and **2** are formed with high yield of 88 and 95%, respectively, but with different nuclearity. Single crystals of **1** were grown by ether diffusion into a CH$_2$Cl$_2$/MeOH solution of **1**. Slow evaporation of a THF solution and ether diffusion of a DMF solution of **2** gave pale-yellow crystals of **2·4THF** or **2·4DMF**, respectively. While dimeric complex **1** is nonemissive, the tetrameric complex **2** shows interesting solid-state photoluminescence.

Scheme 1

Description of Crystal Structure. As shown in Figure 1a, **1** features an interesting dinuclear structure containing two azacrown ether rings, and there is a short intramolecular gold(I)···gold(I) distance of 2.7820-(5) Å. This short gold(I)···gold(I) distance is remarkable when compared to the sum of the van der Waals radii of 3.32 Å,[11] but it is not uncommon for this class of compounds.[4,13] Indeed, the value of 2.7820(5) Å in **1** agrees well with those values of 2.7690(7), 2.7916(12), and 2.7563(3) Å in $[Au(S_2CN(C_5H_{11})_2)_2]$[13] with different solvates and other dinuclear gold(I) dithiocarbamates.[4b] Unlike the linear-chain complex of $[Au(S_2CN(C_5H_{11})_2)_2]$,[13] the close intermolecular gold(I)···gold(I) contact is absent in **1**, and this is most likely ascribed to the bulky azacrown ether rings in the crystal lattice. Notably, the gold(I)···gold(I) distance is ca. 0.32 Å shorter than the value of 3.10 Å for the intramolecular S···S distance of the dithiocarbamate, and this may be recognized as an indication of aurophilic attractions. A weak nonclassical hydrogen-bonding interaction [C(11′)−H(11B′)···O(4): C(11′)−H(11B′) 0.990 Å, H(11B′)···O(4) 2.560 Å, C(11′)·

··O(4) 3.490 Å; C(11′)−H(11B′)···O(4) 163.1°] is also observed in the solid state as shown in Figure 1b. The values of Au(1)−S(1) [2.277(2) Å] and Au(1)−S(2A) [2.273(2) Å] fall in a normal range.[4b,13]

2 crystallizes in two forms: **2·4THF** and **2·4DMF**, which are almost isomorphous. The molecular structure and packing of **2·4THF** as a representative example are shown in Figure 2. The molecular structure of **2** contains a 16-membered ring comprising the gold(I) centers, similar to structures reported by Zanazzi et al.[15] and Jones et al.,[16] which features a tetrameric gold(I) complex with an interesting double-clipped structure built from both thiazole rings and carboxylic acid moieties. The four gold(I) centers form a puckered square with a pseudo symmetry of S_4. The four equivalent gold(I)···gold(I) distances are 3.0478(4) Å for **2·4THF** and 3.0423(4) Å for **2·4DMF**, respectively, which are comparable to the average values of 3.01 Å in $[Au(CH_3CSS)]_4$[15] and of 2.973(1) Å in $[Au(etu-H)]_4$,[16] and significantly shorter than the value of 3.301(5) Å in $[AuCl(pip)]_4$ (pip = piperidine)[25] with four gold(I) centers arranged in a square connected by intermolecular gold(I)···gold(I) interactions. The transannular gold-(I)···gold(I) distance is 4.135 Å, significantly longer than the value of 3.29 Å in $[Au(CH_3CSS)]_4$.[15] Two slipped thiazole rings show the shortest distances of 3.48 Å for **2·4THF** and 3.42 Å for **2·4DMF**, respectively, between the C(N) and C(N) atoms and an almost parallel arrangement, and it is indicative of the possible existence of π···π interactions. Thus, the pucker-squared arrangement for four gold(I) centers may be explained by trying to maximize the π···π interactions for thiazole rings in the solid state. The four THF and DMF solvent molecules are strongly hydrogen-bonded to each SS-COOH moiety between the oxygen atoms of THF or DMF and carboxylic acid moieties [O(2)−H(2A)···O(3): O(2)−H(2A) 0.778 Å, H(2A)···O(3) 1.905 Å, O(2)···O(3) 2.674 Å; O(2)−H(2A)···O(3) 159.0° for **2·4THF** and O(2)−H(2A)···O(3): O(2)−H(2A) 0.820 Å, H(2A)···O(3) 1.810 Å, O(2)···O(3) 2.620 Å; O(2)−H(2A)···O(3) 167.2° for **2·4DMF**] instead of the complementary hydrogen bonding between the carboxylic acid moieties originally expected. Because of the poor solubility, we failed to grow suitable single crystals without any solvate from aprotic solvents or other poor hydrogen-bonding donor solvents. However, the molecular packing of **2·4THF** or
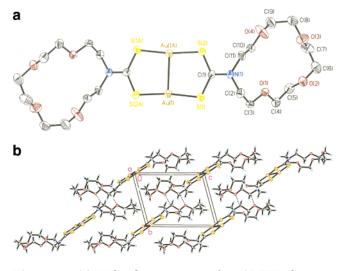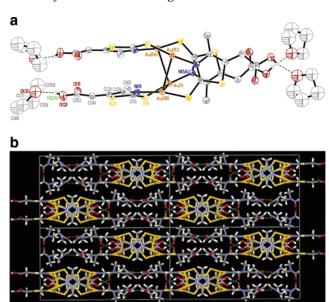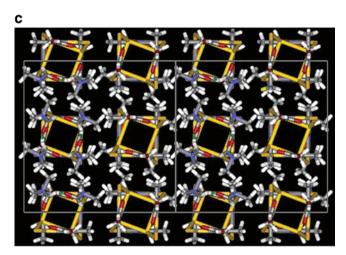
Figure 1. (a) Molecular structure of **1**. ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Au(1)−S(1) 2.277(2), Au(1)−S(2A) 2.273(2), Au(1)···Au(1A) 2.7820(5); S(2A)−Au(1)−S(1) 171.92(7). (b) The molecular packing of **1** with nonclassical hydrogen bonding data for C(11′)−H(11B′)···O(4): C(11′)−H(11B′) 0.990 Å, H(11B′)···O(4) 2.560 Å, C(11′)···O(4) 3.490 Å; C(11′)−H(11B′)···O(4) 163.1°.
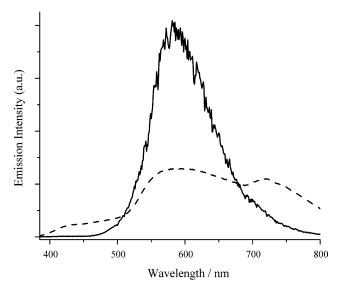
Figure 2. (a) Molecular structure of **2**·4THF. ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (Å) and angles (°) : Au(1)−S(1) 2.255(2), Au(1)−N(1A) 2.059(5), Au(1)···Au(1A) 3.0478(4), Au(1)···Au(1B) 3.0478(4); N(1A)−Au(1)−S(1) 167.55(15). Hydrogen bonding data for O(2)−H(2A)···O(3): O(2)−H(2A) 0.778 Å, H(2A)···O(3) 1.905 Å, O(2)···O(3) 2.674 Å; O(2)−H(2A)···O(3) 159.0°. (b) The molecular packing of **2**·4THF featuring an interesting double-clipped structure with solvated THF molecules. (c) The one-dimensional channel structure is formed when viewing from the *c* axis, where the dotted lines represent weak intermolecular Au···S interactions of 3.800 Å for **2**·4THF (or 3.986 Å for **2**·4DMF). For clarity, the solvates are omitted.

2·4DMF still features an interesting one-dimensional channel structure with the pucker-squared dimension of 3.0478(4) or 3.0423(4) Å, respectively, as shown in Figure 2c. This one-dimensional channel structure may be due to π···π interactions and/or weak intermolecular Au···S interactions of 3.800 Å for **2**·4THF or 3.986 Å for **2**·4DMF, respectively. The values of Au(1)−S(1) [2.256(2) Å] and Au(1)−N(1A) [2.052(5) Å] also fall in a normal range.[15,16] While the tetranuclear complexes of copper(I) or silver(I) are not uncommon,[26] the related gold(I) analogues are still rare.[15,16]

Solid-State Emission Spectra. 2 (without solvates) show interesting solid-state photoluminescence, whereas **1** is nonemissive. Figure 3 shows the solid-state emission spectra of **2** measured at room temperature and at

Figure 3. The solid-state emission spectra of **2** measured at room temperature (dash line) and at 77 K (solid line). Excitation at 355 nm.

77 K. At room temperature, **2** shows low-energy dual emissions with maxima at 585 and 720 nm. Upon cooling to 77 K, **2** shows only a strong emission with a maximum at 585 nm. The emissions at 585 nm are most likely due to a sulfur-to-metal charge-transfer (LMCT, S → Au) transition modified by gold(I)···gold(I) interactions. The emission at 720 nm coming from a metal-centered (5d/6s → 6p) transition is anticipated because of the presence of multiple gold(I)···gold(I) interactions or a gold(I) cluster effect. Similar emission properties have been reported for the [(TPA)AuX] (X = Cl, Br, I; TPA = 1,3,5-triaza-7-phosphaadamantane)[27] and [N4P4-(AuX)₄] (X = Cl, Br, I; N4P4 = 1,4,8,11-tetra(diphenyl-p h o s p h i n o m e t h y l) - 1 , 4 , 8 , 1 1 - tetraazacyclotetradecane)[10b] systems reported by Fackler et al. and Che et al., respectively. In these compounds, the low-energy emissions at 580−674 nm for [(TPA)-AuX][27] and at 600−700 nm for [N4P4(AuX)₄][10b] could come from metal-centered (5d/6s → 6p) transitions, whereas the high-energy ones at 450−491 nm for [(TPA)AuX][27] and at 530 nm for [N4P4(AuX)₄][10b] are most likely due to metal-to-ligand charge-transfer (MLCT, Au → P) transitions. The emission at 720 nm for **2** is comparable to those at 580−674 and 600−700 nm, and thus they are expected to have a similar emission origin due to a metal-centered (5d/6s → 6p) transition. However, the emission at 585 nm is quite red-shifted to those at 530 and 450−491 nm, and this is because the sulfur-to-metal charge-transfer (LMCT, S → Au) transition normally has a lower energy compared to those of metal-to-ligand charge-transfer (MLCT, Au → P) transitions.[28,29]

Conclusion

Self-assembly of (aza-15-crown-5)dithiocarbamate or 2-mercapto-4-methyl-5-thiazoleacetic acid in the presence of NaOMe with gold(I) centers leads to the formation of dinuclear and tetranuclear gold(I) complexes, respectively. **1** features a dinuclear structure containing two azacrown ether rings, and there is a short intramolecular gold(I)···gold(I) distance of 2.7820(5) Å. Impor-

tantly, **2** crystallizes in two forms: **2·**4THF and **2·**4DMF, where the solvent molecules are hydrogen bonded to the carboxylic acid moiety of SSCOOH. **2·**4THF and **2·**4DMF are tetranuclear complexes featuring an interesting double-clipped structure built from both thiazole rings and carboxylic acid moieties. The four gold(I) centers in **2** form a pucker-squared channel with four equivalent gold(I)···gold(I) distances of 3.0478(4) Å for **2·**4THF and 3.0423(4) Å for **2·**4DMF, respectively, and this one-dimensional channel structure may be rationalized by $\pi\cdots\pi$ interactions and/or weak intermolecular Au···S interactions of 3.800 Å for **2·**4THF or 3.986 Å for **2·**4DMF, respectively. Interestingly, with the same synthetic strategy **1** and **2** are formed with different nuclearities. This dramatic different structural motif between **1** and **2** may be ascribed to crystal packing of azacrown ether rings in part. At room temperature, **2** shows low-energy dual emissions with maxima at 585 and 720 nm, whereas it shows only a strong emission with a maximum at 585 nm at 77 K. This interesting luminescence property is suggested to be closely related to aurophilic interactions.

Supporting Information Available: ORTEP (JPG) and CIF files of **2·**4DMF, whose crystal structure is almost isomorphous with that of **2·**4THF, although both contain different solvates. This material is available free of charge via the Internet at http://pubs.acs.org.

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