ORGANOMETALLICS

Volume 20, Number 10, May 14, 2001

Communications

The Close-Knit Supramolecular Network of Bis[(*tert*-butyl isocyanide)gold(I)] 1,3,4-Thiadiazole-2,5-disulfide

James D. E. T. Wilton-Ely, Annette Schier, and Hubert Schmidbaur*

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received February 9, 2001

Summary: Treatment of 2 molar equiv of (^{t}BuNC)AuCl with 1 equiv of the dipotassium salt of 2,5-dimercapto-1,3,4-thiadiazole, K_2(SSS), results in the formation of the crystalline product [(^{t}BuNC)Au]$_2$(SSS) in addition to polymeric material. A crystallographic study reveals a complex supramolecular structure for the crystalline product resembling a "knitted" network containing six independent gold centers.

Aurophilic interactions between two-coordinate gold(I) centers are of increasing interest as a means of designing and constructing supramolecular systems.[1,2] Mononuclear complexes, L−Au−X, generally are found to pair up into dimers (L−Au−X)$_2$ or to form larger oligomers or polymers (L−Au−X)$_n$. The structural motif of the aggregation of the components is determined by the steric and electronic effects of the ligands, with a close approach of gold atoms to an equilibrium distance of 2.9−3.5 Å as the common feature. Ligand redistribution may also occur prior to or during crystallization to give ionic components, $[L_2Au]^+[AuX_2]^-$, which may associate into ion pairs or larger aggregates.[3]

In the present report we describe the preparation and structure of a system in which two (isocyanide)gold(I) units are bound to a common 1,3,4-thiadiazole-2,5-disulfide (SSS) ligand. It represents perhaps one of the most complex arrays of molecules based solely on aurophilic contacts.[4]

Treatment of a dichloromethane solution of 2 molar equiv of [(^{t}BuNC)AuCl] with 1 equiv of K_2(SSS) in methanol afforded a colorless product, [(^{t}BuNC)Au]$_2$($C_2N_2S_3$) (**1**), in ca. 70% yield (Scheme 1). This compound is soluble in di- and trichloromethane but insoluble in pentane. The NMR spectra of these solutions show the ^{1}H and ^{13}C resonances of the isocyanide ligand and the ^{13}C signal of the SSS unit. A strong ν(CN) absorption for the isocyanide ligand is observed in the infrared spectrum at 2232 cm^{-1}. In the FAB mass spectrum the parent ion, *m/z* 710 [M$^+$], can be detected.[5]

Crystals of compound **1** grown from dichloromethane/pentane at −25 °C are monoclinic, in space group $P2_1/n$, with 12 formula units in the unit cell.[6] The

---

(1) (a) Schmidbaur, H. *Chem. Soc. Rev.* **1995**, 391. (b) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11. (c) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3.

(2) (a) Braga, D.; Grepioni; F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375. (b) Bennett, M. A.; Welling, L. I.; Willis, A. C. *Inorg. Chem.* **1997**, *36*, 5670. (c) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, 323.

(3) (a) Bauer, A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 5324 and references therein. (b) Yip, J. H. K.; Feng, R.; Vittal, J. J. *Inorg. Chem.* **1999**, *38*, 3586. (c) Jones, P. G. *Gold Bull.* **1981**, *14*, 102. (d) Ahrland, S.; Dreisch, K.; Norén, B.; Oskarsson, Å. *Mater. Chem. Phys.* **1993**, *35*, 281.

(4) (a) Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch.* **1996**, *51B*, 790. (b) van Calcar, P. M.; Olmstead, M. M.; Balch, A. L. *Chem. Commun.* **1995**, 1773. (c) Mingos, D. M. P.; Yau, J.; Menzer, S.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1894. (d) McArdle, C. P.; Irwin, M. J.; Jennings, M. C.; Puddephatt, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3376.

(5) A solution of commercial K_2(SSS) (35 mg, 0.16 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [(^{t}BuNC)AuCl] (100 mg, 0.32 mmol) in dichloromethane (15 mL). After stirring for 2 h, a fine yellow precipitate was observed. All solvent was removed and the crude residue dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove the yellow solid. After concentration of the solution to a volume of 10 mL, pentane (20 mL) was added carefully to precipitate a colorless crystalline solid, **1**. This was washed with pentane (20 mL) and dried. Yield: 70% (79 mg). IR (KBr disk): 2232 [ν(CN)] cm^{-1}. MS (FAB): *m/z* 710, 6% [M]$^+$. NMR: ^{1}H (CDCl$_3$), 1.58 (s, Me); ^{13}C (CD$_2$Cl$_2$), 166.2 (s, SSS), 140.7 (s, br, *C*N^t-Bu), 59.0 (s, *C*Me$_3$), 29.5 (s, Me). Anal. Calcd for $C_{12}H_{18}Au_2N_4S_3$: C, 20.34; H, 2.56; N, 7.91. Found: C, 20.15; H, 2.37; N, 7.84.

10.1021/om010099y CCC: $20.00 © 2001 American Chemical Society
Publication on Web 04/18/2001

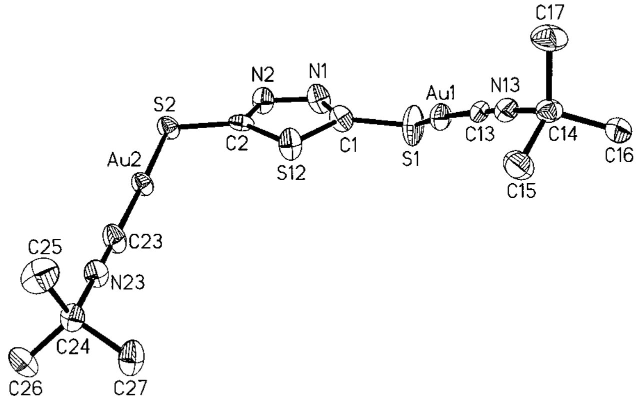
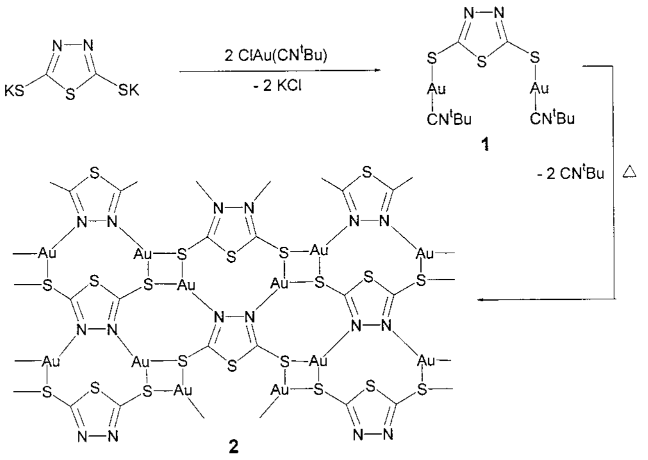


Figure 1. Molecular structure of [(^{t}BuNC)Au]$_2$(SSS) (**1**) (ORTEP drawing with 50% probability ellipsoids). H atoms were omitted for clarity. Only one of the three crystallographically independent molecules is shown; the corresponding values of the other two molecules are given in parentheses. Selected bond lengths (Å) and angles (deg): Au1−S1 = 2.279(2) [2.282(2), 2.285(2)], Au2−S2 = 2.272(2) [2.282(2), 2.281(2)], Au1−C13 = 1.969(8) [1.961(7), 1.974(7)], Au2−C23 = 1.958(7) [1.977(7), 1.971(7)], C13−N13 = 1.126(9) [1.147(9), 1,133(9)], C23−N23 = 1.154(9) [1.141(9), 1.137(9)]; S1−Au1−C13 = 171.7(2) [178.8(2), 178.3(2)], S2−Au2−C23 = 177.2(2) [175.0(2), 173.8(2)], Au1−C13−N13 = 176.5(6) [179.1(6), 179.0(7)], Au2−C23−N23 = 178.7(7) [179.3(7), 176.4(6)], C13−N13−C14 = 174.9(7) [178.0(7), 176.4(8)], C23−N23−C24 = 176.9(8) [178.5(7), 177.5(7)], C1−S1−Au1 = 108.0(3) [106.8(2), 106.5(2)], C2−S2−Au2 = 109.0(2) [107.9(2), 107.1(2)].

Scheme 1. Synthesis of the Complex [(^{t}BuNC)Au]$_2$(SSS) (1) and the Proposed Mode of Formation of an Insoluble Polymer (2) through Elimination of the Isocyanide Ligands



asymmetric unit of the solvent-free lattice contains three nonequivalent dinuclear complex molecules which differ only in conformational details. One representative monomer is shown in Figure 1. The gold cations are all attached to the peripheral sulfide groups of the (SSS) dianion leaving the three heteroatoms of the heterocycle unengaged. The coordination geometry of the metal atoms is close to linear. The atom linkages (S−Au−C) are part of a quasi-linear array of five atoms (S−Au−C−N−C) which has only a slight curvature and is terminated by the *tert*-butyl group at one end and a sharp bending at the sulfur atom at the other (average C−S−Au angle 107.5°). Other details of bond lengths and angles are similar to literature data for (isocyanide)gold(I) complexes.[4,7]

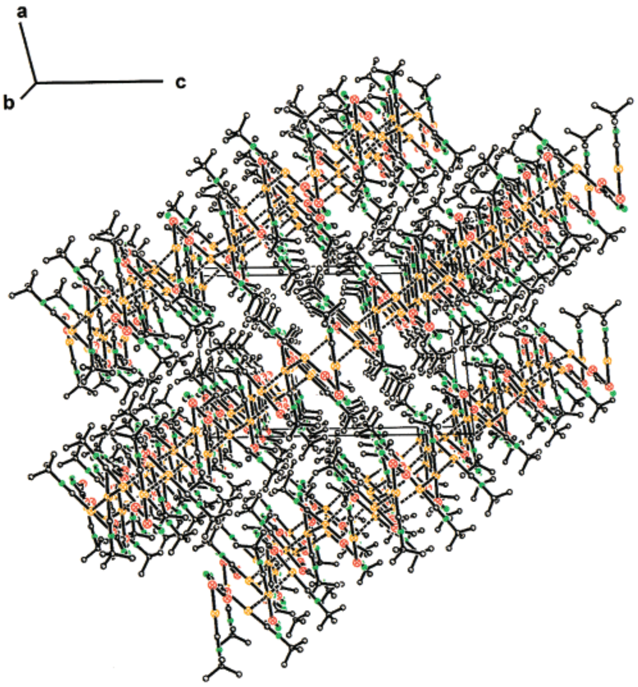


Figure 2. Projection of the extended unit cell for [(^{t}BuNC)Au]$_2$(SSS) (**2**) depicting the layered structure with alternating up/down orientation of the isocyanide ligands. Gold−gold interactions are represented by broken lines, and the principal atoms are color-coded: Au, yellow; N, green; S, red.

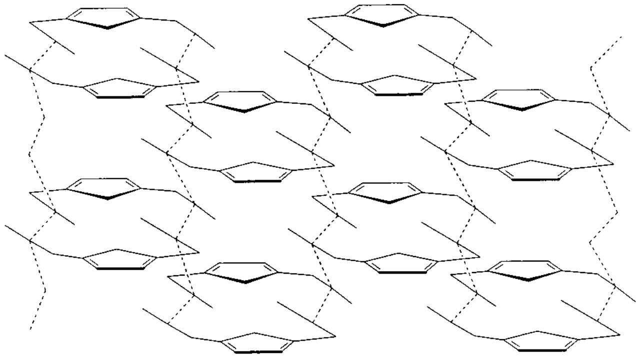
The supramolecular aggregation is based on Au- - -Au contacts between each of the two S−Au−C units of a given molecule and two such units of different neighboring molecules in such a way that the two metal atoms of the reference molecule become part of two different zigzag chains of gold atoms (Chart 1). Neighboring S−Au−C units are "crossed" with dihedral angles S−Au−Au−S in the range between 134.1 and 144.0°. Five of the Au- - -Au distances are short (in the range 3.0447(3)−3.3476(4) Å), while the sixth is significantly longer at 3.4253(3) Å. It was noted[4b] in the past that aurophilic contacts tend to be longer for compounds with isocyanide ligands as compared, for example, to those with phosphine or thioether ligands. This phenomenon

---

(6) **X-ray Crystallography.** A specimen of **1** of suitable quality and size (0.4 × 0.3 × 0.1 mm) of [(^{t}BuNC)Au]$_2$(SSS) was mounted on the end of a quartz fiber in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo Kα radiation. Data were corrected for absorption effects (DELABS from PLATON). The structure was solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all non-hydrogen atoms. All C−*H* atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Crystal data for $C_{12}H_{18}Au_2N_4S_3$: $M_r = 708.42$, colorless crystals, monoclinic, $a = 13.9940(1)$ Å, $b = 18.4157(2)$ Å, $c = 21.9061(2)$ Å, $\beta = 95.244(1)°$, space group $P2_1/n$, $Z = 12$, $V = 5601.7(1)$ Å^3, $\rho_{calcd} = 2.520$ g cm^{-3}, $F(000) = 3888$, $T = -130$ °C, 86 893 measured and 12 224 unique reflections ($R_{int} = 0.0687$), 568 refined parameters, wR2 = 0.0801, R1 = 0.0357 for 11 252 reflections ($I \geq 2\sigma(I)$) used for refinement. Residual electron densities: +1.66/−1.65. The function minimized was $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0$, $b = 34.60$.

(7) (a) Schneider, W.; Bauer, A.; Schmidbaur, H. *Organometallics* **1996**, *15*, 5445. (b) Bauer, A.; Schneider, W.; Schmidbaur, H. *Inorg. Chem.* **1997**, *36*, 2225. (c) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2000**, 3881.

Chart 1. Representation of the Network Formed by $[(^tBuNC)Au]_2(SSS)$ (1) in the Solid State



probably is associated with the strong σ-donor and poor π-acceptor properties of isonitriles. The Au- - -Au distances in the present structure are among the shortest observed for isocyanide complexes.[4] The Au−Au−Au angles in the zigzag chains of metal atoms are either close to linear or close to 90°: Au1, 164.11(1)°; Au2, 81.37(1)°; Au3, 79.04(1)°; Au4, 170.44(1)°; Au5, 79.82(1)°; Au6, 163.67(1)°. The resulting pattern is reminiscent of the structure of polyhalide anions.[8]

The zigzag chains of gold atoms run parallel and are linked via the SSS units, resembling a knitting pattern of “two to the right, two to the left” as illustrated in Chart 1. This network gives thick sheets with the isocyanide ligands pointing in alternation toward the upper and lower interfaces of the layers (Figure 2).

The SSS units appear stacked in pairs, in one of which the heterocycles (connecting the gold atoms Au1/Au2 and Au1′/Au2′) are related by a center of inversion. The other pair (connecting the gold atoms Au3 and Au6 with the gold atoms Au4″ and Au5″) has two crystallographically independent thiadiazole rings, but the arrangement is generally similar to the former.

Single crystals of the compound are stable when stored at low temperature. However, microcrystalline powders lose *tert*-butyl isocyanide, a fact clearly indicated by the distinct isonitrile odor of the samples. Clear solutions in chlorocarbon solvents form a yellow precipitate which cannot then be redissolved. Some of this yellow insoluble material was also observed in the initial stage of the preparation of the ^tBuNC complex. Microanalytical data of the product indicate partial loss of the isocyanide ligand after several weeks at 20 °C, leading to formation of the polymeric disulfide $[Au_2(SSS)]_n$ (**2**). This process (shown in Scheme 1) can be accelerated by refluxing the title compound under anaerobic conditions for 3 h in toluene or by heating the solid under vacuum.[9] A similar degradation was noticed recently for several compounds of the type (RNC)AuSPh by Bachman et al.,[10] where a new luminescent phase of $[PhSAu]_n$ is the final product. The proposed structure **2** with three-coordinate sulfur and gold atoms is based on the known mode of oligomerization of other $(RSAu)_n$ compounds.[11]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie, by the Volkswagenstiftung, by the Alexander von Humboldt Stiftung (J.D.E.T.W.-E.), and by Degussa-Hüls AG.

Supporting Information Available: Tables giving details of the crystal data, data collection, and structure refinement, atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010099Y

---

[8] (a) Raubenheimer, H. G.; Cronje, S. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999; p 557. (b) Schmidbaur, H. *Gmelin Handbook of Inorganic Chemistry*; Springer: Berlin, 1980; Gold, Organic Compounds.

[9] Almost total elimination of the isocyanide ligand was observed. The conditions necessary to remove the remaining approximately 0.1 mol of *tert*-butyl isocyanide resulted in sample decomposition and the appearance of metallic gold. Anal. Calcd for $[C_2N_2S_3Au_2]_n \cdot 0.1C_5H_9N$: C, 5.45; H, 0.16; N, 5.34. Found: C, 5.62; H, 0.20; N, 5.27.

[10] Bachman, R. E.; Bodolsky-Bettis, S. A.; Glennon, S. C.; Sirchio, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 7146.

[11] (a) Schröter, I.; Stähle, J. *Chem. Ber.* **1991**, *124*, 2161. (b) Fackler, J. P., Jr.; van Zyl, W. E.; Prihoda, B. A. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999; p 795.