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Notes

First Example of Linear Strings of Equidistant Gold Atoms in Crystals of $[(2,4,6\text{-}Me_3C_6H_2NC)_2Au]\ [Au(GeCl_3)_2]$

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Introduction

Molecular species with discrete gold−germanium bonds are a new class of bimetallic compounds relevant for a variety of devices with interfaces between gold conductors and germanium-based semiconductors.[1−3] The compounds also show intense luminescence associated with the new (Au)Au−GeX_3 chromophors.[4] Access to this family of complexes is surprisingly facile through the insertion of dihalogermylenes into gold−halogen bonds of $L_nAu{-}X$ molecules (L = neutral donor, X = halogen, $n = 1{-}3$). The resulting complexes appear as neutral, mononuclear molecules $[L_nAuGeX_3]$[2] or as ionic compounds[3] generated in a symmetrization process which leads to various combinations of cations $[LAuL]^+$ and anions $[X_3GeAuGeX_3]^-$. The ionic units are aggregated via interionic, auriophilic[5] (Au−Au) contacts to give tetranuclear complexes[3] in the case of L = Me_2PhP. All these new types of structures were discovered for complexes with tertiary phosphines as ligands L. In the course of our current studies of related isocyanide (isonitrile) compounds,[6] the first example of a self-assembly of the ions to give an infinite gold chain was observed.

Results and Discussion

Synthesis and Characterization. Treatment of (mesitylisonitrile)gold(I) chloride[6] with $GeCl_2$(dioxane) in tetrahydrofuran at −78 °C gives high yields of the 1:1 insertion product **1**, which is obtained in virtually quantitative yield as a pale yellow crystalline material, stable to light, air, and moisture (decomposition temperature 135 °C) and soluble in CH_2Cl_2, $CHCl_3$, and thf. Its analytical and spectroscopic data are in full agreement with the proposed composition (Experimental Section).

$$(2,4,6\text{-}Me_3C_6H_2NC)AuCl + GeCl_2(dioxane) \xrightarrow{thf} (2,4,6\text{-}Me_3C_6H_2NC)AuGeCl_3 + dioxane$$

Crystal and Molecular Structure. Crystals of **1** (from thf/hexane) are monoclinic, space group *C*2/*m*, with $Z = 4$ formula units in the unit cell. The lattice is composed of strings of alternating $[(MesNC)_2Au]^+$ cations and $[Au(GeCl_3)_2]^-$ anions which have close, equidistant contacts Au1−Au2 of 3.402(1) Å at −74 °C (Figure 1). Imposed by crystallographical symmetry, there is equivalent bonding of the two MesNC ligands at Au1 and of the two $GeCl_3$ substituents at Au2 with linear coordination at both gold atoms. The geometrical details of the isocyanide ligands show no anomalies, but there is a slight bending at the isonitrile atoms C and N: N−C−Au1 177.7(6)°; C−N−C1 177.8(6)°.

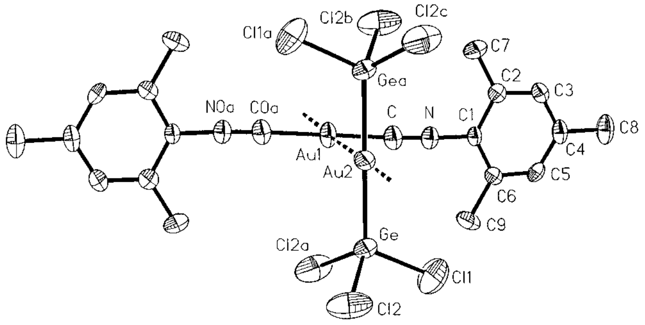

Figure 1. Structure of an ion pair in **1** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Au1−Au2 3.402(1), Au1−C 1.963(6), Au2−Ge 2.3866(7), C−N 1.402(7), Ge−Cl1 2.161(2), Ge−Cl2 2.157(1), C−Au1−C0a 180, Ge−Au2−Gea 180, C−Au1−Au2 90, Ge−Au2−Au1 90, Au1−C−N 177.7(6), C−N−C1 177.8(6).

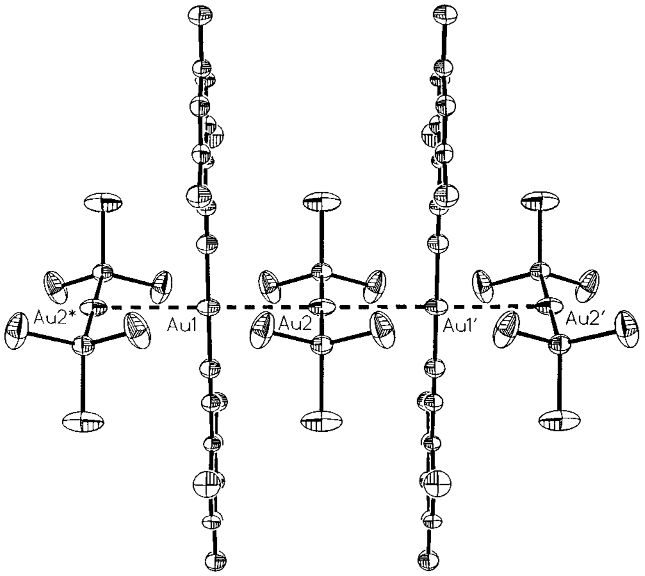

Figure 2. Fraction of the one-dimensional chain structure of **1** with atomic numbering (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond angles (deg): Au2*−Au1−Au2 180, Au1−Au2−Au1′ 180.

The germanium atoms have very narrow Cl−Ge−Cl angles of 101.84(7) (2×, mirror symmetry) and 102.08(10)° (1×) and correspondingly wide Cl−Ge−Au angles of 115.93(4) (2×) and 116.89(8)° (1×), which show a large deviation from the ideal tetrahedral angles. There is precedent for such distortions in the reference compounds with phosphine ligands, and the Au−Ge bonds in **1** [2.3866(7) Å] are also similar to those in other two-coordinate complexes of this type.[2,3]

The strings of gold atoms are linear by symmetry (Figure 2), and are arranged parallel to the crystallographic *b* axis. The Au1−Au2 distances coincide exactly with half the length of

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Table 1. Cell parameters at different temperatures for **1**

temp °C	*a* (Å)	*b* (Å)	*c* (Å)	β [deg]
+21	20.880(1)	6.870(1)	10.972(1)	110.14(3)
−74	20.797(2)	6.804(1)	10.899(1)	109.87(1)
−110	20.741(3)	6.780(1)	10.860(2)	109.79(2)

the *b* axis of the crystal. Therefore a simple measurement of the cell dimensions at different temperatures gives direct access to the temperature dependence of the Au−Au distance (21 °C, 3.435 Å; −74 °C, 3.402 Å; −110 °C, 3.390 Å) (Table 1).

Concluding Remarks. Compound **1** represents the first case of a system with a strictly linear, equidistant chain of gold atoms based solely on weak auriophilicity interactions.[5] Recent quantum chemical calculations[7] for tetranuclear units $\{[L_2\text{-}Au]^+[Au(GeCl_3)_2]^-\}_2$ have demonstrated that very little of the ionic charge is actually localized at the gold atoms reducing Coulomb repulsion between ions of equal charge (two anions or two cations) in the contact region. The aggregation of the ions observed for **1** with its infinite one-dimensional series of intimate metal−metal contacts may therefore also not gain significantly from Coulomb forces between the ions of opposite charge but rather depend largely on the Au−Au attractions.

Experimental Section

General Information. All experiments were carried out in an atmosphere of pure dry nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents were dried and saturated with nitrogen. Standard equipment was used for all preparations and measurements.

Preparation. A solution of (MesNC)AuCl (0.15 g, 0.39 mmol)[6] in thf (10 mL) was treated with small portions of $GeCl_2$(dioxane) (0.09 g, 0.39 mmol) at −74 °C with stirring. After 2 h, the reaction mixture was warmed to 20 °C and the product precipitated by addition of *n*-hexane (yield 0.20 g, 98%; single crystals are grown by carefully layering a thf solution with hexane). ^{1}H-NMR ($CDCl_3$, 20 °C): δ 2.35, s, 3H, *p*-Me; 2.46, s, 6H, *o*-Me; 7.03, s, 2H, *m*-CH. MS(FAB): *m*/*z* 487.5 $[(MesNC)_2Au]^+$, 342.4 $[(MesNC)Au]^+$. Found: C, 23.20; H, 2.18; N, 2.67. $C_{10}H_{11}AuCl_3GeN$ (521.10) requires: C, 23.15; H, 2.13; N, 2.69.

X-ray Structure Determination. A suitable single crystal of **1** was sealed into a glass capillary and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for the compound. Diffraction intensities were corrected for Lorentz polarization and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2.[8] The thermal motion of all non-hydrogen atoms was treated anisotropically. All the hydrogen atoms of the compound were found and isotropically refined. Important interatomic distances and angles are given in the corresponding figure captions. Crystal data of **1**: $C_{10}H_{11}AuCl_3GeN$ (fw 521.10), monoclinic, space group $C2/m$, $a = 20.797(2)$ Å, $b = 6.804(1)$ Å, $c = 10.899(1)$ Å, $\beta = 109.87(1)°$, $V = 1450.4(3)$ Å^3, crystal dimensions 0.06 × 0.07 × 0.30 mm, $Z = 4$, $d_{calcd} = 2.386$ g/cm^{-3}, $F(000) = 960$ e, Enraf Nonius CAD4 diffractometer, MoKα radiation ($\lambda = 0.710\,73$ Å), $T = -74$ °C. Empirical absorption correction [$T_{min} = 0.8418$, $T_{max} = 0.9987$, μ(MoKα) = 127.0 cm^{-1}]; 2768 reflections measured, 1419 unique reflections of which 1255 [$F_o \geq 4\sigma(F_o)$] were "observed"; 123 refined parameters, $wR2$ [unique data] = 0.0489, $R1$ [$F_o \geq 4\sigma(F_o)$] = 0.0222 [$wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$, $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$, $w = q/2\sigma^2(F_o^2) + (ap)^2 + bp$, $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0213$, $b = 2.6993$], $\rho_{final} = +0.55/-0.59$ e Å^{-3} (located at the heavier atoms).

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Supporting Information Available: Tables of crystallographic data including atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen positional parameters and an ORTEP for **1** (8 pages). Ordering information is given on any current masthead page. Atomic coordinates, bond lengths, bond angles, and thermal parameters have also been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request by quoting CSD No. 406600, the names of the authors, and the full journal citation.

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