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Synthesis and Characterization of a Gold Complex Containing $[SbPh]^{2-}$ and $[SbPh_2]^-$ Anions as Bridging Ligands

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The synthesis and structural characterization of the gold antimony complex $[Au_8(SbPh)_2(SbPh_2)_4(PEt_3)_6]$ (**1**) is reported. Complex **1** can be obtained by the reaction of $[AuCl(PEt_3)]$ with a mixture of $PhSb(SiMe_3)_2$ and $Ph_2(SbSiMe_3)$ in presence of the bidentate phosphane ligand dppm [dppm = bis(diphenylphosphanyl)methane]. Complex **1** consists of a distorted heterocubic central $[Au_6Sb_2]$ unit connected to two annulated five-membered rings on two opposite edges. The Au^I ions show weak aurophilic interactions and are bridged by $[SbPh]^{2-}$ and $[SbPh_2]^-$ anions. Despite the high oxidation potential of Au^I, the reaction mixtures and crystals are surprisingly stable.

Introduction

Gold complexes have been the subject of interest over a long period of time and some of the latest investigations focus on the catalytic and pharmaceutical aspects of gold compounds.[1–5] There has also been great interest in the chemistry of gold phosphane complexes and gold chalcogenide clusters.[6–12] However, gold complexes containing heavier group 15 elements are scarce. Recently, Au–As cluster complexes[13,14] were obtained by the synthesis of silylated arsines with Au^I phosphane complexes and a few Au^I complexes with tertiary ligands of the type ER_3 (E = Sb, Bi; R = organic group) are known for antimony,[15–17] but none for bismuth.[18] Only recently, the first Au^I and Cu^I complexes $[Au(C_6F_5)_2][Bi\{C_6H_4(2\text{-}CH_2NMe_2)\}_2]$ and $[(PMe_3)_2CuBi(SiMe_3)_2]$ with a M···Bi interaction (M = Cu, Bi) were reported.[19,20] In contrast, there are several copper and silver antimony clusters.[21–24] The copper antimony clusters, for example $[Cu_{20}Sb_{10}(PCy_3)_8]$, $[Cu_{45}Sb_{16}(PEt_2Me)_{16}]$ and $[Cu_{28}Sb_{12}(PEt_3)_{12}\{Sb(SiMe_3)_2\}_2]$ can be obtained by reactions of Cu^I salts with $Sb(SiMe_3)_3$ in the presence of tertiary phosphanes. The concept of oxidation numbers and localised Cu^I and Cu^{II} centres cannot be applied to these CuSb clusters and they are described as molecular alloys. For silver, molecular alloys were not found. Instead reactions between silver nitrate and $PhSb(SiMe_3)_2$ yielded the silver antimony complexes $[Ag_4(Sb_4Ph_4)_2(PiPr_3)_4]$ and $[Ag_4(Sb_6Ph_6)_2(PnBu_3)_4]$ where oxidation of the antimony precursors to anions with Sb–Sb bonds took place.[24]

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Results and Discussion

Here we report the synthesis of the 12-membered Au–Sb ring $[Au_8(SbPh)_2(SbPh_2)_4(PEt_3)_6]$ (**1**)·$16CH_2Cl_2$ by the reaction of $[AuCl(PEt_3)]$ with a mixture of $PhSb(SiMe_3)_2$ and $Ph_2(SbSiMe_3)$ in presence of the bidentate phosphane ligand dppm [dppm = bis(diphenylphosphanyl)methane] (Scheme 1).

$$[AuCl(PEt_3)] + PhSb(SiMe_3)_2/Ph_2Sb(SiMe_3) \xrightarrow{dppm} [Au_8(SbPh)_2(SbPh_2)_4(PEt_3)_6] \quad (1)$$

Scheme 1. Synthesis of $[Au_8(SbPh)_2(SbPh_2)_4(PEt_3)_6]$ (**1**).

Complex **1** crystallizes from CH_2Cl_2 as yellow blocks in the triclinic space group $P\bar{1}$ (Figure 1) with one molecule in the unit cell and 16 CH_2Cl_2 molecules per unit cell.

The molecular structure of **1** can be described as a 12-membered Au–Sb ring or a distorted heterocubic central $[Au_6Sb_2]$ unit connected to two annulated five-membered rings on two opposite edges. Two gold atoms (Au1, Au1A) are coordinated to a phosphorus atom of triethylphosphane [Au1–P1 2.277(5) Å], whereas the other four gold atoms belong to the nonplanar five-membered rings formed with another four Sb atoms of the $[SbPh_2]^-$ ligands and two further gold atoms [Au4, Au4A]. The bridging angle of the $[SbPh_2]^-$ ligand is about 120° [Au3–Sb3–Au4 118.87(5)°]. Within the peripheral rings the Au4,4A atoms are surrounded by two phosphorus atoms of the phosphane groups and the two antimony atoms of the $[SbPh_2]^-$ ligands in a distorted tetrahedral fashion [P3–Au4–Sb2 108.89(12)°]. Noteworthy structural features are the acute Sb–Au–Sb angle of almost 90° [Sb3–Au4–Sb2 90.50(5)°] and the large P–Au–P angle [P2–Au4–P3 125.25(18)°], which may be the result of steric repulsion of the bulky phosphane ligands. This situation is also reflected in the slightly longer Au–P distance [Au4–P3 2.358(5) Å] relative

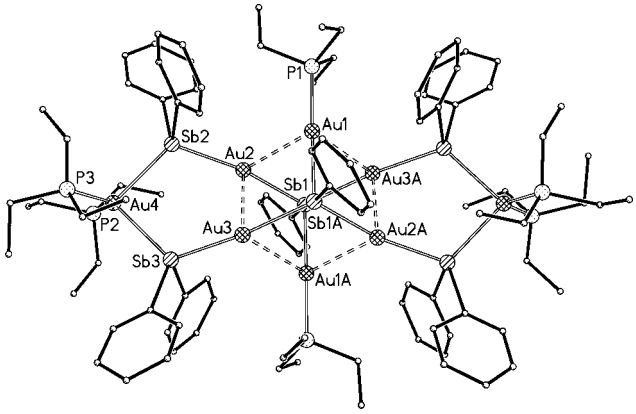

Figure 1. Molecular structure of $[Au_8(SbPh)_2(SbPh_2)_4(PEt_3)_6]$ (**1**) in the solid state [symmetry operation (A) $-x + 1, -y + 1, -z + 1$]. Selected distances [Å] and angles [°]: Au1–Au2 3.0100(10), Au2–Au3 3.0412(17), Au2–Sb2 2.5774(15), Au2–Sb1 2.5883(15), Au3–Sb3 2.5803(12), Au4–Sb3 2.7298(16), Au4–Sb2 2.7350(15), Au1–P1 2.277(5), Au4–P2 2.351(4), Au4–P3 2.358(5), P1–Au1–Sb1A 169.80(11), P1–Au1–Au2 103.92(10), Sb1A–Au1–Au2 83.32(4), P1–Au1–Au3A 102.17(12), Sb1A–Au1–Au3A 84.74(4), Au2–Au1–Au3A 90.48(3), Sb2–Au2–Sb1 167.51(4), Sb2–Au2–Au1 115.45(4), Sb1–Au2–Au1 77.03(3), Sb2–Au2–Au3 93.16(4), Sb1–Au2–Au3 87.47(4), Au1–Au2–Au3 85.21(4), Sb3–Au3–Sb1A 173.68(4), Sb3–Au3–Au2 91.50(4), Sb1A–Au3–Au2 82.56(4), Sb3–Au3–Au1 107.37(4), Sb1A–Au3–Au1A 73.98(3), Au2–Au3–Au1A 81.44(4), P2–Au4–P3 125.25(18), P2–Au4–Sb3 111.05(13), P3–Au4–Sb3 108.74(16), P2–Au4–Sb2 106.81(12), P3–Au4–Sb2 108.89(12), Sb3–Au4–Sb2 90.50(5), Au1A–Sb1–Au2 103.43(5), Au1A–Sb1–Au3A 104.75(5), Au2–Sb1–Au3A 116.13(5), Au2–Sb2–Au4 115.41(5), Au3–Sb3–Au4 118.87(5).

to Au1–P1 with 2.277(5) Å. The same applies to the Au4,4a–Sb bond length, which is the largest observed in **1** [Au4–Sb2 2.7350(15) Å]. Au–Sb bond lengths within the central heterocubic unit are about 0.15 Å shorter [Au2–Sb2 2.5774(15) Å; Sb1–Au3A 2.5903(13) Å]. Au–Sb distances in Au^I stibane complexes are between 2.605 and 2.65 Å.[15–17] If one considers the estimated van der Waals radii of gold (3.6 Å), aurophilic interactions could be expected in compound **1** with Au–Au distances of 3.0100(10) [Au1–Au2] to 3.1773(14) Å [Au3–Au1A].[25] Similar distances are known for other gold compounds, for example the Au–As cluster complexes $[Au_{19}(As\textit{n}Pr)_8(dppe)_6]Cl_3$, $[Au_{10}(As\textit{n}Pr)_4(dppe)_4]Cl_2$ and $[Au_{10}(AsPh)_4(PhAsSiMe_3)_2(P\textit{n}Pr_3)_6]$ or the Au–Se clusters $[Au_{10}Se_4(dpppe)_4]Br_2$ and $[Au_{18}Se_8(dppe)_6]Br_2$ [dppe, dpppe = 1,2-bis(diphenylphosphanyl)ethane or -pentane].[11,13] Aurophilic interactions discussed in the literature for mononuclear gold complexes with Au–Au distances of about 3.05 Å are indicated in **1** by dashed-open bonds (Figure 1).[26] These are longer than Au–Au distances in Au_2(g) (2.472 Å) or the Au–Au distance in cubic close packed gold (2.884 Å).[25]

Contrary to copper or silver complexes with stibido ligands, the Au^I ions in **1** adopt a linear coordination with the Sb anions. Despite the high oxidation potential of Au^I, the reaction mixture and crystals are surprisingly stable, which is also in marked contrast to the silver antimony cluster complexes that decompose at –40 °C.[24] The added phosphane dppm is not found in the solid-state structure of **1**, but it plays an important role in the reaction. If there is no additional phosphane in the mixture, the reaction turns green immediately, indicating a different reaction pathway that is currently being investigated. However, Au–Sb cluster **1** can also be obtained by the reaction with PPh_3 as a stabilizing ligand.

Conclusions

Despite the high oxidation potential of Au^I, the first Au–Sb cluster was described; it was found to exhibit linear coordination of the gold centres to the antimony anions with weak additional aurophilic interactions. The Au–Sb system is surprisingly stable relative to previously described Ag–Sb complexes. With the consideration that gold tends to form Au–Au interactions, further investigations will focus on the synthesis of linked Au–Sb complexes, which may result in novel mixed-metal wires or wires consisting of linked molecular Au–Sb alloys.

Experimental Section

General Remarks: All operations were carried out under an atmosphere of purified nitrogen. CH_2Cl_2 was refluxed over P_2O_5 and freshly distilled prior to use. The dppm ligand was purchased from Sigma–Aldrich. $[AuCl(PEt_3)]$, $PhSbSiMe_3$ and $Ph_2SbSiMe_3$ were prepared according to published procedures.[27,28] The UV/Vis spectrum was recorded in KBr pellets with a Perkin–Elmer Lambda 900 spectrophotometer. Fourier-transform infrared spectroscopy on KBr pellets was performed with a Bruker IFS 28 FTIR instrument.

1: $[AuCl(PEt_3)]$ (0.08 g, 0.228 mmol) was dissolved in CH_2Cl_2 (8 mL) and dppm (0.18 g, 0.456 mmol) was then added. The clear, colourless solution was cooled to –78 °C and $PhSbSiMe_3$/$Ph_2SbSiMe$ (1:1.25, 0.03 mL) was added. The yellow reaction mixture was stored at –78 °C overnight, and then it was warmed up to –40 °C and stored over a period of one week. After one week at –40 °C, yellow crystals of **1** could be isolated for crystallographic measurements. UV/Vis (KBr): λ = 575 (absorption edge) nm. IR (KBr): $\tilde{\nu}$ = 1584.90 (vw), 1571.11 (m), 1474.54 (m), 1428.29 (s), 1377.15 (vw), 1299.70 (vw), 1260.71 (w), 1180.79 (vw), 1155.11 (vw), 1092.43 (m), 1064.44 (w), 1026.97 (m), 1017.86 (m), 996.89 (w), 802.43 (w), 764.14 (w), 741.80 (m), 727.38 (s), 692.96 (vs), 522.49 (m), 506.21 (m), 458.04 (m), 450.2 (m) cm^{-1}.

X-Ray Crystallographic Study: Crystallographic data for the compounds were collected with a STOE IPDS II diffractometer by using graphite-monochromatic Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL software package.[29] Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components were refined with isotropic thermal parameters. **1**: $C_{104}H_{156}Au_8Cl_{16}P_6Sb_6$: M_r = 4465.54; triclinic, space group $P\bar{1}$, Z = 1; a = 14.270(3), b = 15.365(3), c = 18.851(4) Å; α = 105.47(3), β = 90.78(3), γ = 113.47(3)°; V = 3620.0(13) $Å^3$; T = 150(2) K; $F(000)$ = 2080; $\rho_{calcd.}$ = 2.048 $g\,cm^{-3}$; reflections measured 22500, of which 13237 were independent (R_{int} = 0.0899); 603 parameters; wR_2 = 0.2473 (all data); R_1 = 0.0883 [$I > 2\sigma(I)$]; Largest diff. peak and hole 5.289/–3.575 $e\,Å^{-3}$.

CCDC-647732 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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