Gold(I) Complexes with Amine Ligands, I

A Novel Stoichiometry for Chlorogold(I) Complexes: Structure of $L_4Au_3Cl_3$ (L = Pyrrolidine)

Peter G. Jones* and Birte Ahrens

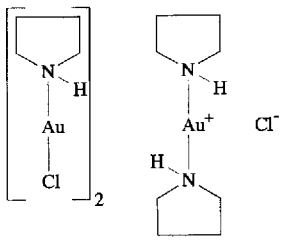
Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

Received August 8, 1997

Keywords: Amines / Gold(I)

The reaction between (tht)AuCl (tht = tetrahydrothiophene) and neat pyrrolidine (L) leads to the compound $L_4Au_3Cl_3$. An X-ray structure determination reveals the presence of molecules LAuCl and ions L_2Au^+ and Cl^-, in the ratio 2:1:1. The packing is characterised by Au···Au contacts and N–H···Cl^- hydrogen bonds.

Gold(I) complexes with amine ligands have not been extensively studied, perhaps because of their limited stability compared to the corresponding phosphane complexes. Apart from cationic complexes $[(phosphane)Au(amine)]^+$, three types of complex with cyclic amines are known: (i) simple covalent molecules LAuCl, e.g. L = piperidine (pip)[1]; (ii) ionic compounds $L_2Au^+Cl^-$, e.g. L = 4-hydroxymethyl-1,5-dimethylimidazole[2]; and (iii) ionic compounds $L_2Au^+AuCl_2^-$, which thus have the same overall stoichiometry as (i), e.g. L = pyridine (py)[3]. The delicate balance between types (i) and (iii) is illustrated by the related imine complexes with L = diphenylmethanimine, for which both types were obtained from the same reaction mixture[4].

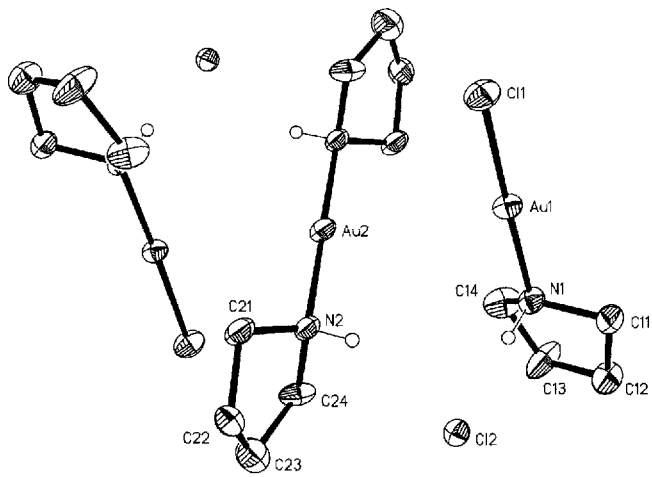


Additionally, gold(I) compounds may exhibit short gold–gold contacts, which are of approximately the same energy as hydrogen bonds and are attributable to relativistic effects ("auxophilicity"[5]); in the above examples, such contacts are observed for pipAuCl (which forms Au_4 squares) and $py_2Au^+AuCl_2^-$ (which contains zigzag Au_4 chains).

We have now begun a systematic study of gold(I) amine complexes. Here we report the preparation and structure of a pyrrolidine complex with the unexpected and unprecedented stoichiometry $L_4Au_3Cl_3$.

The reaction between (tht)AuCl (tht = tetrahydrothiophene) and pyrrolidine afforded a white product, which was recrystallised from dichloromethane/petroleum ether. The results of the crystal-structure analysis show that the compound is in fact 2 (LAuCl)·($L_2Au^+Cl^-$), a mixture of structure types (i) and (iii). Figure 1 shows the formula unit, in which the Au1 atoms (of LAuCl) lie on general positions, the Au2 atom (of L_2Au^+) on an inversion centre, and the chloride anions on twofold axes.

Figure 1. The formula unit of $L_4Au_3Cl_3$ (L = pyrrolidine) in the crystal, showing the atom labelling scheme of the asymmetric unit; the atom Cl2 and its symmetry equivalent lie on twofold axes; C-bonded H atoms are omitted for clarity; ellipsoids represent 50% probability levels



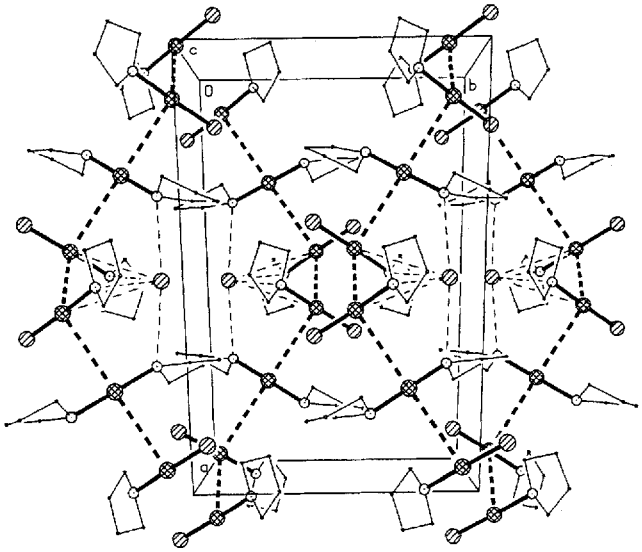
The gold atoms are linearly coordinated [N1–Au1–Cl1 178.5(2)°, N2–Au2–N2 180°]. The Au–N bond lengths of 2.048(6) Å (Au1) and 2.042(6) Å (Au2) are similar to those in pipAuCl [2.068(18) Å][1] and pyAuCl [2.08(3) Å and 2.10(4) Å][3], but longer than in the imidazole complex [2.000(5) and 2.011(5) Å][2] or in $[Au(NH_3)2^+Br^-]$ [2.01(2)–2.03(2) Å][6]. The Au1–Cl1 bond length of 2.257(2) Å is similar to the 2.256(8) Å in pipAuCl[1].

The secondary bonding (Figure 2) is notable. There are two types of gold–gold contacts, 3.2041(7) Å (Au1···Au1′ related by a twofold axis) and 3.5834(4) Å (Au1···Au2)

  0009–2940/97/1212–1813 $ 17.50+.50/0

forming chains with overall direction parallel to (101). The chains are linear at Au2 (by symmetry) but angled at Au1 [131.188(11)°]. Further contacts involve the chloride anions, which are hydrogen-bonded to the NH groups of four ligands, with the following dimensions: N1···Cl2 3.179(6), N2···Cl2 3.284(6) Å, N1–H1···Cl2 172(7), N2–H2···Cl2 153(6), N1–Cl2–N1′ 88.8(2), and N2–Cl2–N2′ 173.6(2)°. The combination of aurophilic and hydrogen bonding has previously been observed by Schmidbaur[7]. Finally, there are very weak contacts of 4.018(2) Å between Cl2 and two Au1.

Figure 2. Packing diagram of $L_4Au_3Cl_3$ (L = pyrrolidine); view parallel to the *z* axis; H atoms are omitted for clarity; radii are arbitrary; thick dashed bonds represent Au···Au interactions, thin dashed bonds secondary interactions involving Cl^- (see text)



We are currently extending our investigations to other (amine)chlorogold(I) species, for which we expect the stoichiometry to be determined, at least in part, by similar systems of secondary bonding.

We thank the *Fonds der Chemischen Industrie* for financial support and Mr. *Andreas Weinkauf* for technical assistance.

Experimental Section

(Pyrrolidine)$_4Au_3Cl_3$: (tht)AuCl (162 mg, 0.5 mmol) was dissolved in neat pyrrolidine (5 ml). The solution was stirred for 1 h with exclusion of light at room temperature; a white precipitate formed. Petroleum ether was added and after cooling for 1 h, the precipitate was filtered off and recrystallized from dichloromethane/petroleum ether to give $L_4Au_3Cl_3$ as colourless crystals, not stable at temperatures >0°C except in the presence of mother liquor; dec. 68 °C. – $C_{16}H_{36}Au_3Cl_3N_4$ (981.74): calcd. C 19.57, H 3.70, N 5.71; found C 19.15 H 3.63 N 5.64. – IR: ν(AuCl) = 348 cm^{-1} w. – ^1H NMR ($CDCl_3$): δ = 1.85 (br., 16 H, β to N in both species), 3.08 (br., 8 H, α to N in L_2Au^+), 3.50 (br., 8 H, α to N in LAuCl). The broad signals imply dynamic processes in solution.

Crystal-Structure Determination of $L_4Au_3Cl_3$: Crystal data: $C_{16}H_{36}Au_3Cl_3N_4$, M_r = 981.74, monoclinic, space group *C2/c*, *a* = 18.250(2), *b* = 11.1156(12), *c* = 13.0643(14) Å, β = 114.835(8)°, *V* = 2405.1(4) $Å^3$, *Z* = 4, D_c = 2.711 Mg m^{-3}, (= 18.6 mm^{-1}, *F*(000) = 1792, *T* = –100 °C. Colourless prism 0.36 × 0.12 × 0.08 mm. Data collection and reduction: The crystal was mounted in inert oil on a glass fibre. Data were collected to $2\theta_{max}$ = 50° using monochromated Mo-K_α radiation (λ = 0.71073 Å) with a Siemens P4 diffractometer fitted with an LT-2 low-temperature attachment. 4277 intensities were collected, of which 2125 (R_{int} = 0.035) were independent. Absorption correction based on ψ scans gave transmission factors of 0.580–0.926. Cell constants were refined from setting angles of 63 reflections in the 2θ range of 6–23°. – The structure was solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-93)[8]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms at N were refined with a restrained N–H bond length, other H using a riding model. The final $wR(F^2)$ was 0.0537 for all data, 128 parameters and 2 restraints, conventional *R*(*F*) = 0.0249, *S* = 0.922, maximum Δρ = 1.162 $eÅ^{-3}$. – Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-100613. Copies may be obtained without charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat. +44(0)1223/336033; E-mail: deposit@chemcrys.cam.ac.uk].

[1] J. J. Guy, P. G. Jones, M. J. Mays, G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1977**, 8–10.
[2] C. J. L. Lock, Z. Wang, *Acta Crystallogr.* **1993**, *C49*, 1330–1333.
[3] H.-N. Adams, W. Hiller, J. Strähle, *Z. Anorg. Allg. Chem.* **1982**, *485*, 81–91.
[4] W. Schneider, A. Bauer, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1997**, 415–420.
[5] [5a] H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11–21. – [5b] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391–400.
[6] D. M. P. Mingos, J. Yau, S. Menzer, D. J. Williams, *J. Chem. Soc., Dalton Trans.* **1995**, 319–320.
[7] W. Schneider, A. Bauer, H. Schmidbaur, *Organometallics* **1996**, *15*, 5445–5446.
[8] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, **1993**.

[97189]