Synthesis and Reactivity of Bimetallic Au–Ag Complexes. *X*-Ray Structure of a Chain Polymer containing the Moiety $\ldots(F_5C_6)_2Au(\mu\text{-}AgSC_4H_8)_2Au(C_6F_5)_2\ldots$

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Summary The 1:1 reaction between $[Bu_4N][Au(C_6F_5)_2]$ and $AgClO_4$ in dichloromethane gives yellow solutions, from which solids of stoicheiometry $Au(C_6F_5)AgL$ can be precipitated by the addition of O, N, S, or P-donors, L; an *X*-ray diffraction study for $L = SC_4H_8$ reveals $[AuAg]_2$ rings linked by Au . . . Au interactions to form infinite metal–atom chains.

The stability of compounds containing M → M′ donor bonds, where M and M′ are transition metals, requires a high electron density on M; the presence or nature of bridging groups between M and M′ seems of minor importance, since compounds with very different bridges are known.

We have chosen the anion $[Au(C_6F_5)_2]^-$ as a metal centre M and have tried to form M → M′ bonds by allowing the salt $[Bu_4N][Au(C_6F_5)_2]$ to react with $AgClO_4$, according to equation (1). This reaction leads to a yellow solution.

$$[Bu_4N][Au(C_6F_5)_2] + AgClO_4 \rightarrow [Bu_4N]ClO_4 + Au(C_6F_5)_2Ag \quad (1)$$

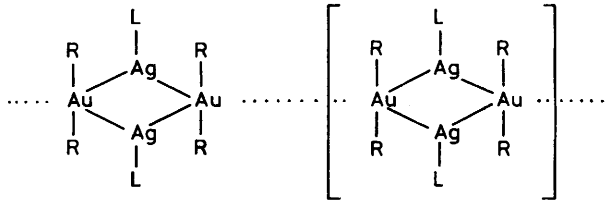
Addition of stoicheiometric amounts of L (L = tetrahydrothiophen, pyridine, pyridine *N*-oxide, or PPh_2Me) then results in a yellow or orange precipitate of formula $Au(C_6F_5)_2AgL$. These complexes are insoluble in non-complexing solvents but soluble in donor solvents, forming pale solutions in which the presence of the $[Au(C_6F_5)_2]^-$ anion was confirmed by i.r. spectroscopy.

Addition of a further mole of L to a suspension of $Au(C_6F_5)_2AgL$ in dichloromethane forms silver salts of the $[Au(C_6F_5)_2]^-$ anion, equation (2), as was confirmed by

$$Au(C_6F_5)_2AgL + L \rightarrow [AgL_2]^+[Au(C_6F_5)_2]^- \quad (2)$$

analysis, i.r. spectroscopy, and conductivity studies (1:1 electrolytes). A similar process probably occurs in the donor solvents mentioned above.

We have prepared single crystals of the tetrahydrothiophen complex $Au(C_6F_5)_2AgSC_4H_8$ (**1**; R = C_6F_5, L = SC_4H_8) and have determined its *X*-ray structure.



(A)

(1)

Crystal data: $C_{16}H_8AgAuF_{10}S$, $M_r = 727{\cdot}13$, orthorhombic, space group *Pccn*, $a = 11{\cdot}185(3)$, $b = 22{\cdot}475(6)$, $c = 14{\cdot}802(4)$ Å, $U = 3721$ Å^3, $Z = 8$, $D_c = 2{\cdot}60$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å), $\mu = 91$ cm^{-1}, $F(000) = 2688$. 3265 unique reflexions in the range $7° < 2\theta < 50°$ were measured on a Stoe four-circle diffractometer. After Lorentz, polarization, and absorption corrections (crystal size $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}15$ mm) 2005 reflexions with $F > 4\sigma(F)$ were used for all calculations. The structure was solved by the heavy-atom method and refined (Au, Ag, and S anisotropic) to $R = 0{\cdot}053$, $R_w = 0{\cdot}051$.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

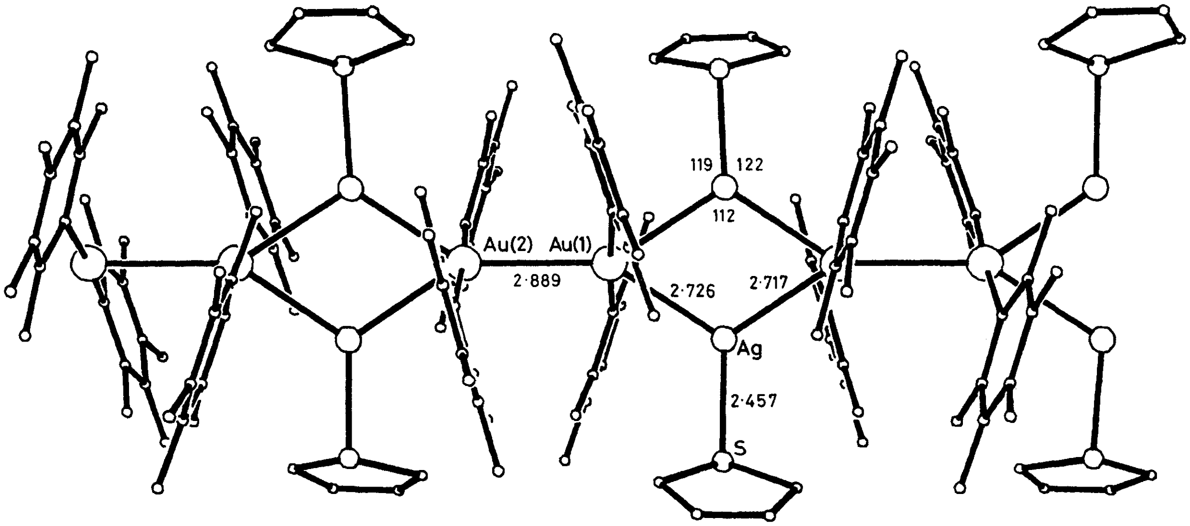

FIGURE. Part of the infinite chain structure of $Au(C_6F_5)_2AgSC_4H_8$, showing bond lengths (Å) and angles (deg.). The two independent gold atoms lie on the twofold axis 0·25, 0·25, *z*. The C–Au–C moieties are inclined to each other at an angle of 52°.

TABLE. I.r. frequencies (cm^{-1}) of $[Au(C_6F_5)_2]$ groups.

$[Bu_4N][AuR_2]$	780s	950vs, br
$R_2AuAgSC_4H_8$	786s	969vs, 955sh
$R_2AuAg(py)$	789s	965vs
$R_2AuAg(Opy)$	789s	971vs, 961sh
$R_2AuAgPPh_2Me$	787s	965vs, 961sh

The moiety (A) is repeated through short Au . . . Au contacts[1,2] [2·889(2)Å], thus forming infinite chains of metal atoms (Figure). The geometry and i.r. frequencies (see Table) of the AuR_2 groups of (A) are very similar to those of the free anion $[Au(C_6F_5)_2]^-$.[3] The Au–Ag bond lengths are 2·717, 2·726(2) Å. A possible simplified model of the bonding is that each gold atom (acting as donor) forms two donor–acceptor bonds to the $[Ag–L]^+$ centres, in which the silver acts as an sp^2-hybridised Lewis acid. The electrons of these bonds are located primarily on the gold atom and, being mainly of d character, are of low stereochemical significance; the C–Au–C bond angles are thus scarcely affected [176, 177(1)° in two independent anions].

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