Reactions of Carbonylchlorogold(I) with Thiolates and Thiols. Crystal and Molecular Structures of $[NaL(H_2O)][(AuCl)_3SBu^t]$, $[NaL][AuCl_2]$, $[NaL]_4[AuCl_2]_2[Au_4Cl_6S_2]$ and $[NaL]_2[Au_4Cl_6S_2]$ (L = 1,4,7,10,13-pentaoxacyclopentadecane)†

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By the reaction of [AuCl(CO)] with the thiols RSH (R = Bu^t, $C_6H_3Me_2$-2,6 or C_6F_5) amorphous gold(I) thiolates Au(SR) were obtained. With 2,6-dimethylbenzenethiolate under CO at atmospheric pressure in CH_2Cl_2 as solvent, gold metal and RSSR were formed, while with H_2S amorphous Au_2S was the product. The reaction of [AuCl(CO)] with [Na(15-crown-5)][SBu^t] in 1:1 ratio yielded [Na(15-crown-5)(H_2O)][$(AuCl)_3SBu^t$] **1** and [Na(15-crown-5)][$AuCl_2$] **2** (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane). The crystal structure of **1** revealed that the anionic part contains three AuCl groups co-ordinated to the Bu^tS^- ligand forming a tetrahedral arrangement around the sulfur. The $[AuCl_2]^-$ anions in **2** are co-ordinated through the chlorine atoms to two $[Na(15\text{-crown-}5)]^+$ cations; thus, the sodium cation has a distorted pentagonal-pyramidal co-ordination to five oxygen atoms of the crown ether with the axial position occupied by the chlorine atoms of the $AuCl_2^-$ anion. The reaction of [AuCl(CO)] with [Na(15-crown-5)][SBu^t] in 3:1 molar ratio afforded the mixed-valence Au^I–Au^{III} complexes $[Na(15\text{-crown-}5)]_4[AuCl_2]_2[Au_4Cl_6S_2]$ **3** and $[Na(15\text{-crown-}5)]_2[Au_4Cl_6S_2]$ **4**. Their crystal structures revealed that in the $[Au_4Cl_6S_2]^{2-}$ anion two $AuCl_2$ units are connected by the sulfur atoms of two SAuCl groups forming a centrosymmetric planar $Cl_2Au(\mu\text{-}S)_2AuCl_2$ skeleton. The structure of **3** also contains linear $[AuCl_2]^-$ anions.

Carbonylchlorogold(I), [AuCl(CO)], is a stable mononuclear compound[1] for which a convenient synthetic route has become available.[2] It is an attractive starting material for the preparation of co-ordination compounds of gold. We report here the reactions with sulfur-containing reagents.

At the onset of this work several reaction pathways were anticipated to be possible in principle between [AuCl(CO)] and H_2S, RSH or RS^- (R = alkyl or aryl). Particularly interesting would be simple substitution of the chloride ligand by thiolate, by which a carbonyl derivative of gold(I) with an anionic ligand different from halide could be obtained. Earlier work[3] had shown that carbonyl complexes of gold(I) are well established for chloride both in the solid state and in solution, and for bromide only in solution, the stability with respect to CO dissociation and AuX formation decreasing in the sequence Cl > Br > I; the same hierarchy of stability was established for the carbonyl complexes of platinum(II)[4] and palladium(II).[5]

Recently, the reactivity of [AuCl(CO)] with sulfur-containing ligands has been shown[6] to proceed both by chloride and carbonyl substitution, in the formation of the hexanuclear $[Au_6(SC_6H_2Pr^i_3\text{-}2,4,6)_6]$ from 2,4,6-triisopropylbenzenethiol; moreover, oxidation of gold(I) to gold(III) was found[7] in the reaction of [AuCl(CO)] with PhS_2Ph.

Experimental

All the operations were carried out under an atmosphere of dinitrogen or carbon monoxide, as specified. Solvents were dried by conventional methods; Na(SBu^t) was prepared according to the literature.[8] 1,4,7,10,13-Pentaoxacyclopentadecane (15-crown-5) was dried under an inert atmosphere with activated molecular sieves or distilled prior to use; both treatments were later found to be unsatisfactory, as shown by the presence of water in the structure of compound **1**. The IR spectra in the 4000–400 cm^{-1} region were measured with Perkin-Elmer model 283 B or FT-IR 1725 X instruments and the mass spectra with a TSQ 70 Finnigan spectrometer.

Reactions of [AuCl(CO)].—*With thiols* RSH (R = Bu^t, $C_6H_3Me_2$-2,6 *or* C_6F_5). The compounds Au(SBu^t) and Au($SC_6H_3Me_2$-2,6) were synthesized by adding liquid $HSBu^t$ (0.525 cm^3, 4.66 mmol), $HSC_6H_3Me_2$-2,6 (0.240 cm^3, 1.78 mmol) or HSC_6F_5 (0.450 cm^3, 3.37 mmol) at solid-CO_2 temperature under an atmosphere of N_2 to [AuCl(CO)] (1.213 g, 4.66 mmol; 0.459 g, 1.76 mmol; or 0.874 g, 3.36 mmol respectively) in toluene (120, 75 or 80 cm^3 respectively). Control IR spectra at low temperature did not show the presence of carbonyl bands different from that of [AuCl(CO)] at 2161 cm^{-1}. At *ca.* +10 °C precipitation of the insoluble thiolato complexes began. The colourless amorphous products were filtered off, dried *in vacuo* and sealed in ampoules. With $HSBu^t$ the yield was substantially quantitative (Found: C, 17.0; H, 3.0; Au, 67.3. C_4H_9AuS requires C, 16.7; H, 3.2; Au, 68.8%). The reaction with 2,6-dimethylbenzenethiol gave the corresponding gold(I) thiolate (yield 80%) (Found: C, 28.1; H, 2.5; Au, 58.0; S, 8.4. C_8H_9AuS requires C, 28.7; H, 2.7; Au, 58.9; S, 9.6%). IR (Nujol mull): 1580w, 1165m-w, 1040m, 1025m, 987w, 765s, 725m, 708m, 687w, 583w and 463w cm^{-1}. Analogously, the pentafluorophenyl derivative was obtained

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

(yield 85%) from the reaction with HSC_6F_5 (Found: C, 18.4; S, 8.4. C_6AuF_5S requires C, 18.2; S, 8.1%). IR: 1640m, 1515s, 1485s, 1405w, 1145m, 1090s, 1010m, 985s, 850s, 718w and 625w cm^{-1}.

With H_2S. Gaseous H_2S was allowed to diffuse slowly through a fritted disc in a reactor containing a solution (25 cm^3) of [AuCl(CO)] (0.720 g, 2.76 mmol) in CH_2Cl_2 at solid-CO_2 temperature. The formation of HCl and CO in the gas phase (IR spectroscopy) and of a greenish suspension, which finally turned deep brown, was observed. The precipitate was filtered off and dried under reduced pressure (0.481 g, 82% yield) at room temperature (Found: Au, 92.3. Calc. for Au_2S: Au, 92.5%). A Guinier photograph of the product showed five very weak lines due to gold metal.

With 2,6-*dimethylbenzenethiol under* CO. The reaction of [AuCl(CO)] (1.256 g, 4.82 mmol) with the thiol (0.65 cm^3, 4.83 mmol) at about −65 °C using CH_2Cl_2 as solvent (100 cm^3) under CO at atmospheric pressure failed to give the gold(I) thiolato complex obtained in toluene under N_2; instead, formation of both gold metal (0.902 g, 95% yield) and the disulfide $(SC_6H_3Me_2\text{-}2,6)_2$ [Found: C, 69.0; H, 6.6. $C_{16}H_{18}S_2$ requires C, 70.0; H, 6.6%). Mass spectrum (most abundant peaks): *m*/*z* 136.2 and 273.9].

With $Au(SBu^t)$. The compound [AuCl(CO)] (0.339 g, 1.30 mmol) was added to a suspension of $Au(SBu^t)$ (0.37 g, 1.30 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C under CO; the resulting suspension slowly evolved CO and in about 12 h an apparently homogeneous brown precipitate was observed. The solution was colourless and carbonyl compounds (IR spectroscopy) or other gold-containing compounds (qualitative tests) were no longer present. The precipitate was filtered off, washed with CH_2Cl_2 (10 cm^3) and dried *in vacuo* (0.456 g). Gas chromatography–mass spectrometry (temperature programming from 80 to 250 °C) on the solution: unique peak at 23.65 min. Mass spectrum (main peaks): *m*/*z* 57, 104, 112, 113, 149, 168, 219 and 279 (Found for organic phase after removal of solvent: C, 82.0; H, 13.3; Cl, 1.0; S, 3.1%).

With $Na(SBu^t)$ *in the presence of* 15-*crown*-5. By operating under CO, to a CH_2Cl_2 (100 cm^3) solution of [AuCl(CO)] (0.98 g, 3.77 mmol) were added equimolar quantities of $Na(SBu^t)$ and 15-crown-5 (the latter dried over molecular sieves) in the same solvent (50 cm^3). After stirring for some hours, a brown precipitate, which was filtered off, and a yellow brown solution were obtained. The solution, which showed no IR carbonyl stretching vibrations, was kept at about 4 °C for several days; by addition of heptane, two distinctly different types of crystals separated out as pale yellow needles and colourless plates. The crystals were selected by hand and further characterized by X-ray diffraction methods. The colourless and pale yellow crystals were found to be $[Na(15\text{-crown-}5)(H_2O)][(AuCl)_3SBu^t]$ **1** and $[Na(15\text{-crown-}5)][AuCl_2]$ **2** respectively, from X-ray diffraction analysis (see below).

With 15-*crown*-5–NaCl (1 : 1). In an attempt to synthesize compound **2**, a CH_2Cl_2 (25 cm^3) solution of [AuCl(CO)] (1.112 g, 4.27 mmol) was treated at room temperature with equimolar quantities of NaCl and 15-crown-5 in the same solvent (10 cm^3), under N_2. Gas evolution and disappearance of the band at 2161 cm^{-1} of [AuCl(CO)] were noted. A small amount of an unidentified brown solid was filtered off and the yellow solution was partially evaporated under reduced pressure. Two solid phases crystallized, a colourless one (**2**) and yellow prisms, which were not further characterized. Both species had almost identical IR spectra with the typical bands of the crown ether, 15-crown-5.

Isolation of $[Na(15\text{-crown-}5)]_4[AuCl_2]_2[Au_4Cl_6S_2]$ **3** *and* $[Na(15\text{-crown-}5)]_2[Au_4Cl_6S_2]$ **4**.—By operating under dinitrogen, in an attempt to synthesize compound **1**, [AuCl(CO)] (1.096 g, 4.21 mmol) dissolved in CH_2Cl_2 (20 cm^3) was treated with $Na(SBu^t)$ (0.157 g, 1.4 mmol) and an equimolar quantity of distilled 15-crown-5 (0.31 g, 1.4 mmol) corresponding to an Au : S molar ratio of 3 : 1. The IR carbonyl band of [AuCl(CO)] disappeared only after stirring the reaction mixture for about 2 d. The suspension was filtered and heptane added. Crystallization of three products was observed: **2** and two others, namely yellow prisms of **3** and orange prisms of **4**, as shown by the subsequent X-ray diffraction analysis.

X-Ray Crystallography.—All the X-ray experiments were carried out with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation (λ = 0.710 69 Å).

$[Na(15\text{-crown-}5)(H_2O)][(AuCl)_3SBu^t]$ **1**. A transparent crystal of $[Na(15\text{-crown-}5)(H_2O)][(AuCl)_3SBu^t]$ **1** with approximate dimensions 0.2 × 0.3 × 0.5 mm was mounted on a glass rod at room temperature. The lattice parameters (see Table 5) of the monoclinic crystal with the space group $P2_1/c$ (no. 14) were refined using 25 reflections in the range $7.2 < \theta < 15.1°$. The data collection with ω scans at 18 °C between $\theta = 3$ and 28° resulted in 6969 intensity values. During the data collection three intensity-control reflections were monitored every hour, showing no loss of intensity. The structure was solved by direct methods[9] and subsequent Fourier-difference syntheses.[10] Refinement of the structural model using *F* values, with isotropic thermal parameters for all except the H atoms converged to $R = 0.084$.[10] An empirical absorption correction with the program DIFABS[11] and merging improved the *R* value to 0.070, by using 2436 unique reflections with $I > 3\sigma(I)$. Anisotropic thermal parameters were assigned to all except the H atoms and further refinement of the extinction coefficient[12] gave the final *R* value of 0.043 ($R' = 0.050$). Hydrogen atoms were included at geometrically calculated positions in the calculation of the structure factors. Details of the crystal data and structure refinement are in Table 5 and positional parameters in Table 6.

$[Na(15\text{-crown-}5)][AuCl_2]$ **2**. Compound **2** crystallizes as pale yellow needles. One with approximate dimensions 0.20 × 0.20 × 0.50 mm was selected and mounted on a glass rod. Data were obtained at −60 °C using ω–2θ scans in the range $3 < \theta < 33°$ in the same way as for compound **1** (Table 5). From the two possible orthorhombic space groups *Pmmn* (no. 59) and $Pmn2_1$ (no. 31), the non-centrosymmetric one was confirmed during the refinement of the structure. A Patterson synthesis[9] revealed the coordinates of the gold and chlorine atoms. After completing the structural model with Fourier-difference syntheses the refinement, based on F^2, converged to $R_1 = 0.043$.[13] Hydrogen atoms were treated as for **1**. The absolute structure was determined: $R_1 = 0.036$, Flack parameter of 0.0010 (wrong configuration $R_1 = 0.057$, Flack parameter 1.0309).[13] Positional parameters are in Table 7.

$[Na(15\text{-crown-}5)]_4[AuCl_2]_2[Au_4Cl_6S_2]$ **3**. A yellow crystal of compound **3** with the approximate dimensions 0.05 × 0.1 × 0.3 mm was mounted on a glass rod. The determination of the lattice parameters and the intensity measurements at −50 °C was carried out in the range $3 < \theta < 29°$ as for compound **1** (Table 5). The structure was solved and refined as for **1**, converging to $R = 0.114$.[10] After absorption correction,[11] anisotropic thermal parameters were assigned to the Au, Cl, S and Na atoms. The H atoms were calculated at their ideal positions but not included in the refinement, resulting in $R = 0.060$ ($R' = 0.075$). Positional parameters are in Table 8.

$[Na(15\text{-crown-}5)]_2[Au_4Cl_6S_2]$ **4**. An orange crystal of compound **4** with the approximate dimensions 0.05 × 0.3 × 0.2 mm was mounted on a glass rod. The determination of the lattice parameters (Table 5), data collection in the range $3 < \theta < 30°$ at −60 °C and the solution of the structure by Patterson synthesis was carried out as for **1**. Refinement[10] of the structural model with *F* values, and with anisotropic thermal parameters for all except the H atoms, resulted in $R = 0.032$. Taking account of the extinction coefficient and with the H atoms at their geometrically calculated positions, the final value $R = 0.029$ ($R' = 0.037$). Positional parameters are in Table 9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The reaction of [AuCl(CO)] with thiols RSH did not result in the formation of [Au(SR)(CO)]. Rather, the substantially insoluble thiolato complexes Au(SR) (R = Bu^t, $C_6H_3Me_2$-2,6 or C_6F_5) were obtained according to stoichiometry (1). No

$$[AuCl(CO)] + RSH \xrightarrow[\text{toluene}]{N_2} Au(SR) + HCl + CO \quad (1)$$

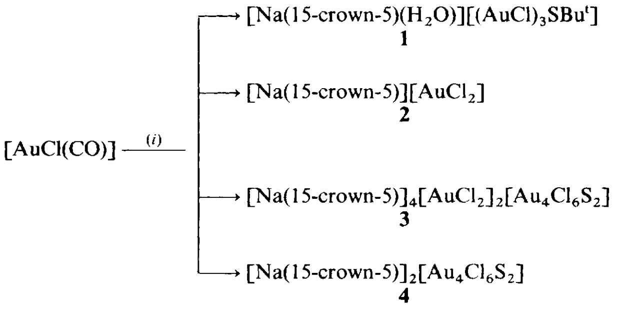
products different from [AuCl(CO)] were detected spectroscopically in the IR carbonyl stretching region either at low or at room temperature. Thiolato complexes of gold(I) are normally prepared by treating solutions of $[AuCl_4]^-$ with RSH or with $[AuCl\{S(CH_2CH_2OH)_2\}]$ or by reaction of $[AuCl(AsPh_3)]$ with $SiMe_3(SR)$.[14] The formation of these products under the conditions described in this paper represents an alternative method of preparation from anhydrous reagents in a dry solvent. No crystalline product was isolated, as shown by the absence of lines in the X-ray powder diagrams.

Although reaction (1) did not lead to any detectable gold carbonyl product, it is quite reasonable to assume that the formation of gold metal observed under the conditions specified in equation (2) (R = $C_6H_3Me_2$-2,6) may occur through the

$$[AuCl(CO)] + RSH \xrightarrow[CH_2Cl_2]{CO} Au + HCl + CO + \tfrac{1}{2}RSSR \quad (2)$$

transient formation of an unstable carbonylgold thiolate [Au(SR)(CO)] undergoing reductive elimination of diaryl disulfide. Carbon monoxide is present in both reactions (1) and (2); in fact, in (2), the higher vapour pressure of the solvent probably results in a partial pressure of CO evolved which is similar, at least at room temperature, to that of the experiment described by (1) carried out in toluene (CO is evolved in the reaction). This suggests that a specific role in the reaction is played by the solvent. Aromatic hydrocarbons are known[15] to give adducts with silver(I); thus, it is reasonable to assume that toluene may enter the co-ordination sphere of gold too, competing with CO and stabilizing a gold(I) intermediate [Au(SR)L] (L = CO or η^2-C_6H_5Me).

In principle, the reaction of H_2S with [AuCl(CO)] could give either $[AuCl(SH_2)]$ or [Au(SH)(CO)]. The former would correspond to a hydrogensulfide complex and the latter a product of halide substitution by H_2S giving the gold-co-ordinated SH group and HCl. Examples of co-ordination of both H_2S and HS are known.[16] In view of the unsuccessful attempts to isolate intermediate carbonyl derivatives of gold(I) in the reactions with RSH and H_2S, we reckoned that the use of the thiolate anions SR^- could in principle lead to nucleophilic attack on the carbonyl carbon of [AuCl(CO)]. Complexation of Na(SR) by a crown ether was expected to increase the nucleophilicity of the thiolate anion and thus favour the reaction. The reaction of [AuCl(CO)] with [Na(15-crown-5)]-[SBu^t] in CH_2Cl_2 gives four products **1**–**4** identified by X-ray crystallography, as shown in Scheme 1. Products **1**, **3** and **4** derive from complexation of the Bu^tS^- to gold(I), without (**1**) or with (**3** and **4**) cleavage of the S–R bond, and giving partial (products **3** and **4**) oxidation of gold(I) to gold(III). Product **2** clearly arises from substitution of CO in [AuCl(CO)] by Cl^-, the latter presumably arising from adventitious hydrolysis of [AuCl(CO)] or by reaction of Bu^tS^- with the solvent. It was also isolated from the reaction of NaCl with [AuCl(CO)] in the presence of 15-crown-5. The crystal structures of the four products have some interesting features, which deserve some comments.



Scheme 1 (*i*) [Na(15-crown-5)][SBu^t], CH_2Cl_2

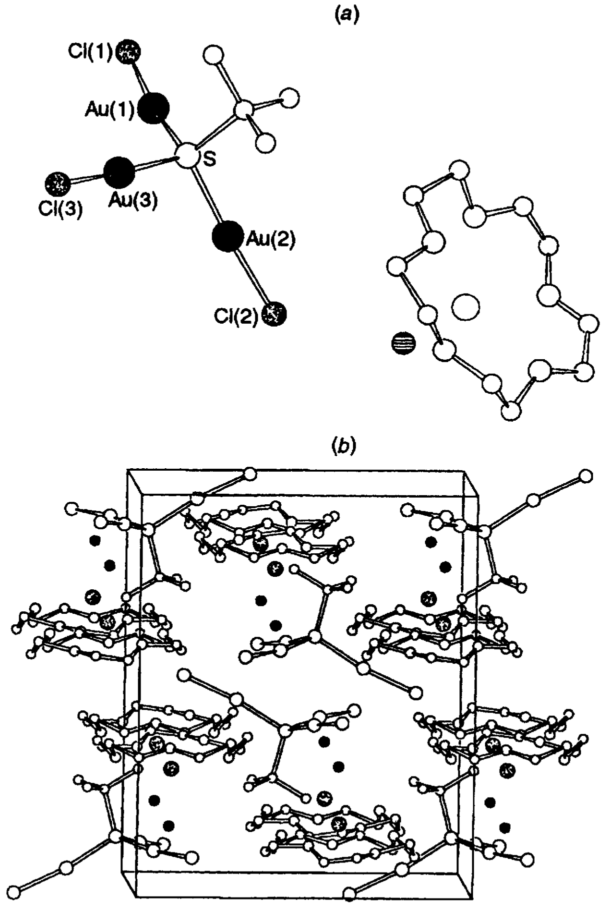


Fig. 1 Structure of complex **1**: (*a*) labelling scheme, (*b*) unit cell showing the mutually staggered arrangement of the $[(AuCl)_3SBu^t]^-$ anions

Structures of the Gold Derivatives.—The structure of compound **1** is built up by the $[Na(15\text{-crown-}5)(H_2O)]^+$ cation and by the trinuclear complex anion $[(AuCl)_3SBu^t]^-$, see Fig. 1(*a*). The cations as well as the anions are related by a centre of symmetry to form pairs [Fig. 1(*b*)]. In the case of the anionic pairs, the AuCl groups are in a staggered arrangement such that the Au atoms form a distorted octahedron with interatomic distances ranging from 3.326 to 3.686 Å. The Au···Au distances are larger than 3.32 Å, above the value for attractive interactions. On the other hand this arrangement may be a favourable one for an intermolecular redox disproportionation to yield Au metal and the mixed-valence complex $[Cl_2Au^{III}$-$(\mu\text{-}SAu^ICl)_2Au^{III}Cl_2]^{2-}$ (see below).

Table 1 Bond distances (Å) and angles (°) for [Na(15-crown-5)-(H_2O)][$(AuCl)_3SBu^t$] **1**

Au(1)–S	2.262(6)	Na–O(1)	2.32(3)
Au(2)–S	2.257(2)	Na–O(2)	2.39(2)
Au(3)–S	2.248(2)	Na–O(3)	2.44(3)
Au(1)–Cl(1)	2.265(8)	Na–O(4)	2.38(4)
Au(2)–Cl(2)	2.248(9)	Na–O(5)	2.41(3)
Au(3)–Cl(3)	2.257(9)	Na–O(11)	2.27(2)
S–C(11)	1.91(2)		
Cl(1)–Au(1)–S	172.2(3)	O(1)–Na–O(11)	102.0(9)
Cl(2)–Au(2)–S	175.7(1)	O(2)–Na–O(11)	119.1(9)
Cl(3)–Au(3)–S	173.1(1)	O(3)–Na–O(11)	105.6(9)
Au(1)–S–C(11)	108.3(8)	O(4)–Na–O(11)	111(2)
Au(2)–S–C(11)	108.3(3)	O(5)–Na–O(11)	102(2)
Au(3)–S–C(11)	107.9(3)	Au(1)–S–Au(2)	111.1(9)
O(1)–Na–O(2)	69(2)	Au(2)–S–Au(3)	109.8(1)
O(1)–Na–O(5)	68.4(9)	S–C(11)–C(12)	105(1)
O(2)–Na–O(3)	69(1)	S–C(11)–C(13)	106(2)
O(3)–Na–O(4)	71(1)	S–C(11)–C(14)	107(2)
O(4)–Na–O(5)	66(1)	Au(1)–S–Au(3)	111.5(9)

Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 2 Bond distances (Å) and angles (°) for [Na(15-crown-5)]-[$AuCl_2$] **2**

Au–Cl(1)	2.261(3)	O(2)–C(2)	1.429(9)
Au–Cl(2)	2.252(3)	O(2)–C(3)	1.418(10)
Cl(1)–Na	2.734(6)	O(3)–C(4)	1.50(2)
Na–O(1)	2.336(8)	O(3)–C(5)	1.310(14)
Na–O(2)	2.356(6)	C(1)–C(2)	1.502(10)
Na–O(3)	2.317(10)	C(3)–C(4)	1.518(13)
O(1)–C(1)	1.431(8)	C(5)–C(5′)	1.45(2)
Cl(1)–Au–Cl(2)	178.4(2)	Na–O(2)–C(2)	112.1(5)
Au–Cl(1)–Na	100.85(13)	Na–O(2)–C(3)	109.1(5)
Cl(1)–Na–O(1)	112.1(2)	C(2)–O(2)–C(3)	113.5(6)
Cl(1)–Na–O(2)	97.0(2)	Na–O(3)–C(4)	108.9(6)
Cl(1)–Na–O(3)	107.5(3)	Na–O(3)–C(5)	118.6(8)
O(1)–Na–O(2)	71.7(2)	C(4)–O(3)–C(5)	116.2(9)
O(2)–Na–O(2′)	143.3(3)	O(1)–C(1)–C(2)	106.1(6)
O(2)–Na–O(3)	71.5(3)	O(2)–C(2)–C(1)	108.4(5)
O(3)–Na–O(3′)	134.5(3)	O(2)–C(3)–C(4)	108.6(7)
Na–O(1)–C(1)	108.7(4)	O(3)–C(4)–C(3)	98.5(9)
C(1)–O(1)–C(1′)	115.7(7)	O(3)–C(5)–C(5′)	113.4(6)

Primed atoms are related by the symmetry transformation $-x, y, z$.

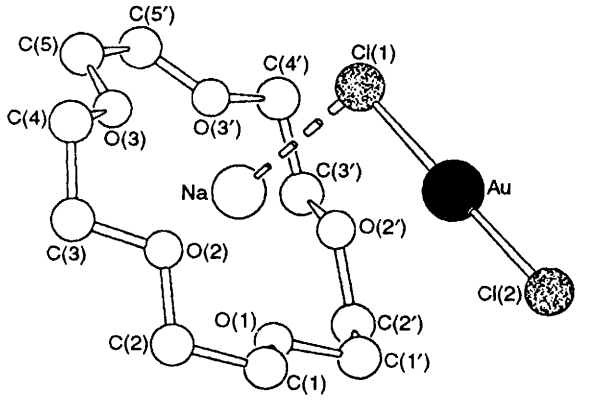


Fig. 2 Structure and labelling scheme for compound **2**

Table 3 Bond distances (Å) and angles (°) for [Na(15-crown-5)]$_4$-[$AuCl_2$]$_2$[$Au_4Cl_6S_2$] **3**

Au(1)–Cl(11)	2.34(1)	Na(1)–O(10)	2.39(3)
Au(1)–Cl(12)	2.31(1)	Na(1)–O(11)	2.36(3)
Au(1)–S	2.30(1)	Na(1)–O(12)	2.39(3)
Au(1′)–S	2.31(2)	Na(1)–O(13)	2.35(3)
Au(2)–Cl(2)	2.24(1)	Na(1)–O(14)	2.32(4)
Au(2)–S	2.24(2)	Na(2)–O(20)	2.35(4)
Au(3)–Cl(31)	2.23(2)	Na(2)–O(21)	2.42(4)
Au(3)–Cl(32)	2.26(1)	Na(2)–O(22)	2.34(3)
Cl(31)–Na(2)	2.74(3)	Na(2)–O(23)	2.41(3)
Cl(32)–Na(1)	2.73(2)	Na(2)–O(24)	2.37(3)
Cl(11)–Au(1)–Cl(12)	95.4(5)	Au(1)–S–Au(2)	100.3(4)
Cl(11)–Au(1)–S	173.8(4)	Au(1)–S–Au(2′)	97.0(4)
Cl(11)–Au(1)–S′	90.5(4)	Au(1)–S–Au(1′)	96.6(4)
Cl(12)–Au(1)–S	90.8(4)	Au(3)–Cl(31)–Na(2)	86.9(5)
Cl(12)–Au(1)–S′	174.0(4)	Cl(31)–Au(3)–Cl(32)	178.2(4)
S–Au(1)–S′	83.4(4)	Au(3)–Cl(32)–Na(1)	82.8(5)
Cl(2)–Au(2)–S	178.0(4)		

Primed atoms are related by the symmetry transformation $1 - x, 1 - y, 1 - z$.

Table 4 Bond distances (Å) and angles (°) for [Na(15-crown-5)]$_2$[$Au_4Cl_6S_2$] **4**

Au(1)–Cl(2)	2.332(3)	Na(1)–O(10)	2.427(7)
Au(1)–Cl(3)	2.328(3)	Na(1)–O(11)	2.392(7)
Au(1)–S(1)	2.308(2)	Na(1)–O(12)	2.366(7)
Au(1)–S(1′)	2.313(2)	Na(1)–O(13)	2.406(8)
Au(2)–Cl(1)	2.282(2)	Na(1)–O(14)	2.332(8)
Au(2)–S(1)	2.247(3)	Na(1)–Cl(1)	2.659(5)
Cl(2)–Au(1)–Cl(3)	94.23(9)	Au(1)–S(1)–Au(1′)	97.09(9)
Cl(2)–Au(1)–S(1)	91.17(9)	Au(1)–S(1)–Au(2)	101.2(1)
Cl(2)–Au(1)–S(1′)	174.06(9)	Au(1)–S(1′)–Au(2′)	96.13(8)
Cl(3)–Au(1)–S(1)	174.04(9)	O(10)–Na(1)–O(11)	68.3(2)
Cl(3)–Au(1)–S(1′)	91.71(8)	O(10)–Na(1)–O(14)	69.8(2)
S(1)–Au(1)–S(1′)	82.91(9)	O(11)–Na(1)–O(12)	70.6(2)
Cl(1)–Au(2)–S(1)	177.28(9)	O(12)–Na(1)–O(13)	71.3(2)

Primed atoms are related by the symmetry transformation $-x, -y, -z$.

The thiolate ligand of [$(AuCl)_3SBu^t$]$^-$ bridges three AuCl units forming a tetrahedral arrangement $RSAu_3$. A sulfur–gold cluster to three gold atoms was found by Jones *et al.*[17] for the cationic complex [{$Au(PPh_3)$}$_3$S]$^+$. Within the $RSAu_3$ tetrahedron the C(11)–S–Au bond angles in the range 107.9(3)–108.3(8)° and the Au–S–Au angles between 109.8(1) and 111.5(9)° (Table 1) are close to the ideal values for sp^3 hybridization. On the contrary, the bond angles[17] Au–S–Au in [{$Au(PPh_3)$}$_3$S]$^+$ (82.9–87.7°) are much smaller and indicate S–Au bonding with substantially unhybridized p orbitals. The S–Au bond lengths of 2.248(2)–2.262(6) Å in **1** are in the expected range for covalent single bonds[18] and only slightly shorter[17] than in [{$Au(PPh_3)$}$_3$S]$^+$. Normal values for covalent single bonds[18] are also found for the Au–Cl distances between 2.248(9) and 2.265(8) Å. The monovalent gold atoms are almost linearly co-ordinated with S–Au–Cl bond angles between 172.2(3) and 175.7(1)°.

The Na^+ cations in [Na(15-crown-5)(H_2O)]$^+$ exhibit a six-fold co-ordination of a pentagonal pyramid with the five oxygen atoms of the crown ether forming the base and the water ligand in the axial position. The shortest Na–O distance of 2.27(2) Å, approximating the sum of the ionic radii of Na^+ and O^{2-} (2.35 Å),[18] is to the water molecule. The distance to the O atoms of the crown ether, on the contrary, are significantly longer between 2.32(3) and 2.44(3) Å. The anionic part of **1** contains a substantially tetrahedral sulfur atom co-ordinated to a tertiary butyl group and to three gold atoms. Four-co-ordinated sulfur atoms are not so frequently encountered in inorganic chemistry, especially in complexes containing alkanethiolate ligands. Examples are the manganese(I) dialkyl sulfide-bridged complex [$(OC)_2(cp)Mn(\mu\text{-}SMe_2)Mn(cp)(CO)_2$] (cp = $\eta\text{-}C_5H_5$)[19] and the more recent sulfide ligand four-

Table 5 Crystal data and data collection details

	[Na(15-crown-5)(H$_2$O)]-[(AuCl)$_3$SBu^t] **1**	[Na(15-crown-5)][AuCl$_2$] **2**	[Na(15-crown-5)]$_4$[AuCl$_2$]$_2$-[Au$_4$Cl$_6$S$_2$] **3**	[Na(15-crown-5)]$_2$-[Au$_4$Cl$_6$S$_2$] **4**
Formula	$C_{14}H_{31}Au_3Cl_3NaO_6S$	$C_{10}H_{20}AuCl_2NaO_5$	$C_{40}H_{80}Au_6Cl_{10}Na_4O_{20}S_2$	$C_{20}H_{40}Au_4Cl_6Na_2O_{10}S_2$
M	1047.41	511.13	2573.48	1551.22
Crystal habit and colour	Yellow plates	Pale yellow needles	Yellow prisms	Orange prisms
Space group	$P2_1/c$, monoclinic	$Pmn2_1$, orthorhombic	$P2_1/c$, monoclinic	$P\bar{1}$, triclinic
a/Å	12.948(3)	12.3966(10)	9.714(3)	7.761(3)
b/Å	13.057(6)	7.5144(10)	28.192(9)	11.052(5)
c/Å	15.840(3)	8.5983(10)	12.931(3)	11.539(5)
α/°	—	—	—	84.56(2)
β/°	93.127(9)	—	91.70(2)	88.37(2)
γ/°	—	—	—	78.53(2)
Z	4	2	2	1
U/Å^3	2672.1	801.0(2)	3549.0	965.7
D_c/g cm^{-3}	2.599	2.119	2.408	2.667
F(000)	1912	836	2400	712
μ(Mo-Kα)/cm^{-1}	168.228	–	128.552	157.098
Minimum, maximum and average absorption corrections	0.7289, 1.1131, 0.9624	–	0.4337, 1.3771, 0.9719	0.8195, 1.4271, 1.0179
h,k,l intervals	0–17, 0–17, −20 to 20	0–11, −13 to 13, −18 to 18	0–13, 0–38, −17 to 17	0–10, −15 to 15, −16 to 16
Independent reflections (R_{int})	6689 (0.052)	3115 (0.069)	9584 (0.091)	5561 (0.026)
Measured reflections	6969	6382	10 103	5944
Reflections with $I > 3\sigma(I)$[a]	2436	2744	2411	4311
Weighting scheme	$1/\sigma^2$	SHELX 93	$1/\sigma^2$	$1/\sigma^2$
Refined variables	254	96	220	200
R[b]	0.043	0.036	0.060	0.029
R'[c]	0.050	0.097[d]	0.075	0.037
Maximum (Δ/σ)	0.20	0.03	0.00	0.003
Residual density/e Å^{-3}	0.983	1.981	1.263	1.981
Secondary extinction coefficient[12]	8.5926×10^{-9}	—	—	5.75×10^{-8}

[a] Only the reflections with $I > 3\sigma(I)$ were used for the refinement. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$. [d] $R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

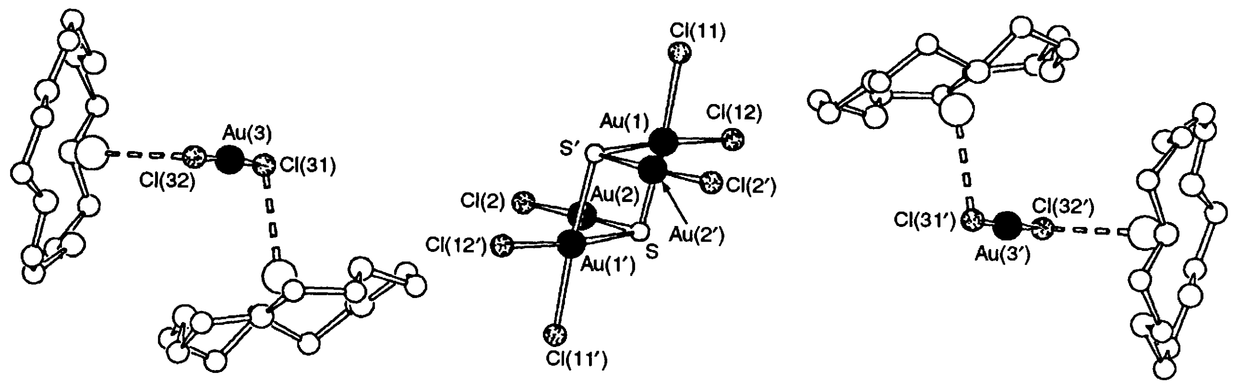


Fig. 3 Structure and labelling scheme for compound **3**

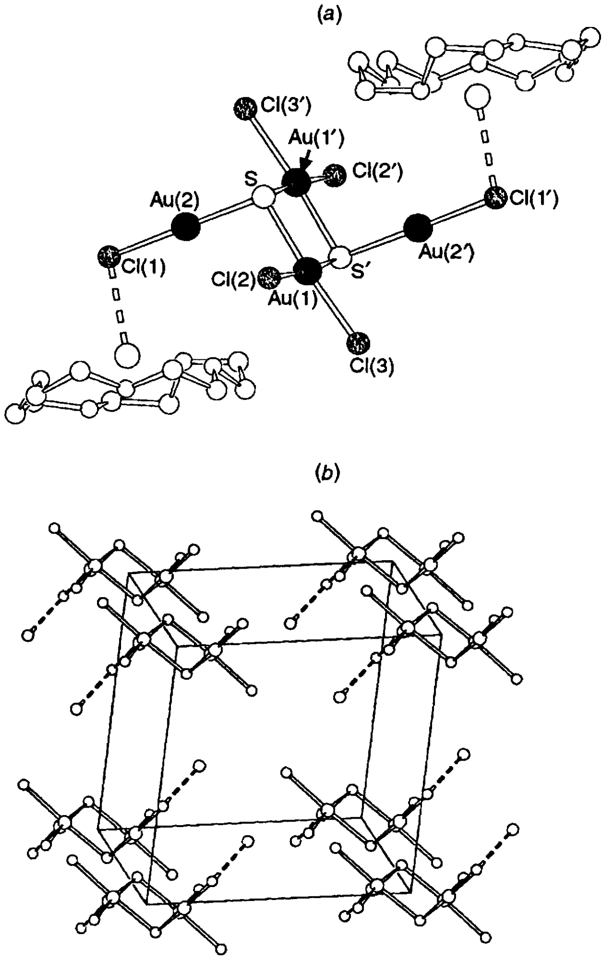


Fig. 4 Structure of compound **4**: (*a*) labelling scheme, (*b*) unit cell

co-ordinated to $(Ph_3P)Au^+$ groups in $[\{Au(PPh_3)\}_4S][O_3SCF_3]_2{\cdot}2CH_2Cl_2$.[20]

The co-ordination of the Na^+ cation in compound **2** is similar to that in **1**. In this case the axial position of the pentagonal pyramid is occupied by a chlorine atom of the $[AuCl_2]^-$ anion. The corresponding Na–Cl(1) distance 2.734(6) Å is equal to the sum of the ionic radii[18] and indicates a strong interaction. The Na–O distances ranging from 2.317(10) to 2.356(6) Å to the oxygen atoms of the crown ether in the equatorial position of the pentagonal pyramid are comparable to the values in **1**. The $[AuCl_2]^-$ anion, see Fig. 2 and Table 2, exhibits the expected linear geometry with a Cl–Au–Cl bond angle of 178.4(2)° and bond distances of 2.261(3) and 2.252(3) Å. In **2** the cation and the anion occupy mirror planes of the space group $Pmn2_1$. In the

Table 6 Positional parameters for $[Na(15\text{-crown-}5)(H_2O)][(AuCl)_3SBu^t]$ **1**

Atom	*x*	*y*	*z*
Au(1)	0.517 18(8)	0.187 58(8)	0.959 04(6)
Au(2)	0.652 15(8)	0.036 81(8)	1.094 14(6)
Au(3)	0.368 89(8)	0.066 14(8)	1.091 59(7)
Cl(1)	0.536 6(8)	0.344 3(6)	1.019 3(5)
Cl(2)	0.805 0(6)	0.115 0(8)	1.080 5(6)
Cl(3)	0.233 6(7)	0.175 4(7)	1.081 8(6)
S	0.498 4(4)	0.042 4(5)	0.881 7(3)
Na	−0.026 1(9)	−0.099 8(9)	0.683 9(7)
O(1)	0.014(2)	0.069(2)	0.653(2)
O(2)	0.138(2)	−0.088(2)	0.623(1)
O(3)	0.043(2)	−0.268(2)	0.651(1)
O(4)	1.162(2)	0.298(2)	0.880(2)
O(5)	0.822(2)	−0.496(2)	1.138(2)
O(11)	0.967(2)	−0.096(2)	0.826(1)
C(1)	0.105(4)	0.098(3)	0.612(2)
C(2)	0.175(3)	0.012(3)	0.643(3)
C(3)	0.199(3)	−0.175(3)	0.642(2)
C(4)	0.137(3)	−0.271(3)	0.611(2)
C(5)	1.039(4)	0.173(2)	0.892(2)
C(6)	1.135(3)	0.193(3)	0.859(2)
C(7)	1.263(2)	0.349(4)	0.885(2)
C(8)	1.250(2)	0.449(4)	0.900(3)
C(9)	0.840(3)	−0.599(3)	1.134(3)
C(10)	0.935(3)	−0.621(4)	1.117(3)
C(11)	0.497(2)	0.078(2)	0.765(1)
C(12)	0.601(2)	0.135(2)	0.754(1)
C(13)	0.484(2)	−0.022(2)	0.716(1)
C(14)	0.408(2)	0.152(2)	0.748(2)

Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 7 Atomic coordinates for $[Na(15\text{-crown-}5)][AuCl_2]$ **2**

Atom	*x*	*y*	*z*
Au	0	0.2959(1)	0.9981(1)
Cl(1)	0	0.5209(4)	1.1727(3)
Cl(2)	0	0.0775(5)	0.8189(5)
Na	0	0.3348(6)	0.4459(6)
O(1)	0	0.0275(9)	0.4050(8)
O(2)	0.1804(4)	0.2372(7)	0.4339(6)
O(3)	0.3998(8)	0.5038(13)	0.1244(11)
C(1)	0.4023(6)	0.0206(9)	0.8270(9)
C(2)	0.3119(7)	−0.0476(11)	0.9267(9)
C(3)	0.2399(7)	0.3130(10)	0.5582(10)
C(4)	0.2860(8)	0.4898(16)	0.0670(14)
C(5)	0.4417(9)	0.3585(15)	0.1831(12)

Table 8 Positional parameters for $[Na(15\text{-crown-}5)]_4[AuCl_2]_2[Au_4Cl_6S_2]$ **3**

Atom	*x*	*y*	*z*
Au(1)	0.404 6(2)	0.519 27(6)	0.601 8(1)
Au(2)	0.271 6(2)	0.437 00(6)	0.424 2(1)
Au(3)	0.848 5(2)	0.198 53(6)	0.445 3(1)
Cl(2)	0.167(1)	0.366 4(4)	0.416 3(8)
Cl(11)	0.458(1)	0.527 6(4)	0.778 3(8)
Cl(12)	0.182(1)	0.547 3(4)	0.611 4(9)
Cl(31)	0.620(1)	0.195 7(5)	0.427 7(9)
Cl(32)	1.080(1)	0.201 8(4)	0.457 6(9)
S	0.376(1)	0.507 9(4)	0.426 3(7)
Na(1)	1.058(1)	0.106 2(5)	0.425(1)
Na(2)	0.650(2)	0.231 8(6)	0.234(1)
O(10)	1.245(3)	0.084 1(9)	0.539(2)
O(11)	0.976(2)	0.081 0(9)	0.586(2)
O(12)	0.859(2)	0.057 1(8)	0.402(2)
O(13)	1.010(3)	0.095 7(9)	0.247(2)
O(14)	1.262(4)	0.104(1)	0.336(3)
O(20)	0.464(4)	0.282(1)	0.194(3)
O(21)	0.705(3)	0.312 2(9)	0.284(2)
O(22)	0.865(3)	0.254 3(9)	0.175(2)
O(23)	0.747(3)	0.168(1)	0.135(2)
O(24)	0.472(3)	0.192(1)	0.139(2)
C(10)	1.203(6)	0.089(2)	0.638(4)
C(11)	1.070(4)	0.070(2)	0.665(3)
C(12)	0.869(4)	0.047(1)	0.581(3)
C(13)	0.773(4)	0.060(2)	0.488(3)
C(14)	0.792(4)	0.071(1)	0.304(3)
C(15)	0.893(4)	0.063(2)	0.222(3)
C(16)	1.120(6)	0.081(2)	0.191(4)
C(17)	1.250(6)	0.098(2)	0.229(4)
C(18)	1.383(5)	0.094(2)	0.391(4)
C(19)	1.361(5)	0.102(2)	0.500(4)
C(20)	0.465(5)	0.316(2)	0.271(4)
C(21)	0.593(4)	0.348(1)	0.263(3)
C(22)	0.835(4)	0.330(1)	0.251(3)
C(23)	0.929(4)	0.289(1)	0.239(3)
C(24)	0.942(4)	0.214(1)	0.147(3)
C(25)	0.861(5)	0.185(2)	0.077(3)
C(26)	0.637(6)	0.141(2)	0.078(5)
C(27)	0.535(8)	0.171(3)	0.046(6)
C(28)	0.363(6)	0.225(2)	0.098(5)
C(29)	0.338(5)	0.258(2)	0.183(4)

Table 9 Positional parameters for $[Na(15\text{-crown-}5)]_2[Au_4Cl_6S_2]$ **4**

Atom	*x*	*y*	*z*
Au(1)	−0.055 02(4)	0.550 89(3)	0.356 80(3)
Au(2)	0.376 48(4)	0.407 42(3)	0.437 19(3)
Cl(1)	0.590 1(3)	0.244 4(2)	0.392 0(2)
Cl(2)	0.076 1(3)	0.664 5(2)	0.211 4(2)
Cl(3)	−0.291 2(3)	0.537 6(2)	0.241 9(2)
S	0.160 3(3)	0.561 6(2)	0.487 2(2)
Na(1)	0.429 4(4)	0.143 1(3)	0.237 0(3)
O(10)	0.692 0(8)	0.088 6(5)	0.118 9(5)
O(11)	0.415 2(7)	0.272 2(5)	0.057 8(5)
O(12)	0.145 2(8)	0.268 6(6)	0.216 8(6)
O(13)	0.227 7(9)	0.047 4(6)	0.358 2(6)
O(14)	0.489 4(8)	−0.069 1(5)	0.216 9(6)
C(11)	0.699(1)	0.170 0(9)	0.014 0(8)
C(12)	0.586(1)	0.293 1(9)	0.032 8(8)
C(13)	0.286(1)	0.383 2(8)	0.076 0(8)
C(14)	0.119(1)	0.341 8(9)	0.108 2(8)
C(15)	0.013(1)	0.200(1)	0.248(1)
C(16)	0.054(1)	0.127(1)	0.360(1)
C(17)	0.229(1)	−0.072 9(9)	0.325(1)
C(18)	0.415(1)	−0.135 7(9)	0.311(1)
C(19)	0.675(1)	−0.113 0(9)	0.204(1)
C(20)	0.734(1)	−0.039 5(9)	0.099 0(9)

case of the cation the mirror plane runs through atoms Na and O(1) as well as through the midpoint of the C(5)–C(5′) bond, while the anion lies with all three atoms on the mirror plane.

Compounds **3** and **4**, see Figs. 3 and 4, Tables 3 and 4, respectively, have structures closely related to each other and differ only in the fact that in **3** a $[Na(15\text{-crown-}5)](AuCl_2)$ group is included in the asymmetric unit together with half a $[Na(15\text{-crown-}5)][Cl_2Au(\mu\text{-}SAuCl)]$ group. Such an arrangement of different gold species with different oxidation states in the same unit cell is documented in the literature, for example in $Cs_2Au_2Cl_6$,[21] $Rb_3Au_3Cl_8$,[22] $Rb_2Au_3Br_6$[22] and Au_4Cl_8.[23] In both centrosymmetric compounds **3** and **4** the inversion centre lies in the middle of the planar arrangement $Au^{III}(\mu\text{-}S)_2Au^{III}$. The geometrical parameters of the $Au_4Cl_6S_2{}^{2-}$ groups in both structures are essentially equal and, in particular, the $Au(1)(\mu\text{-}S)_2Au(1')$ group is planar, as required by the inversion centre. On the basis of the hybridization at the trivalent gold, Au(1) or Au(1′) should also lie in a plane; in fact it lies 0.012 Å only out of the plane formed by Cl(11), Cl(12), S and S′ (in **3**). The angles at the sulfur atoms, 96.13(8)–101.2(1)° in **4** and 96.6(4)–100.3(4)° in **3**, are intermediate between those in compound **1** (close to sp^3 hybridization) and in the $[\{Au(PPh_3)\}_3S]^+$ cation[17] (close to those expected for the use of pure p orbitals). The Au^{III}–S distances [2.30(1) in **3** and 2.308(2) Å in **4**] are similar to those in $[\{Au(PPh_3)\}_3S]^+$ and the Au^I–S distances [2.24(2) in **3** and 2.247(3) Å in **4**] to those in **1**. The Au^{III}–Cl distances are relatively long, in the range 2.31(1)–2.34(1) Å in comparison with the corresponding distances (terminal) in Au_2Cl_6[24] (2.25 and 2.23 Å) or in the $[AuCl_4]^-$ anion of $Rb_3Au_3Cl_8$[22] (2.28 and 2.29 Å) or in Au_4Cl_8[23] [2.24(2) and 2.26(1) Å]. In **3**, parallel to the observation in **2**, the two Cl atoms in the $[AuCl_2]^-$ anion, Cl(31) and Cl(32), are still co-ordinatively bonded to the sodium cations in the 15-crown-5 moiety: the Na–Cl(31) [2.74(3) Å] and Na–Cl(32) distances [2.73(2) Å] are virtually identical; in this case, however, the arrangement of the crowns around the $[AuCl_2]^-$ anion is not symmetrical (angle between the two crowns approximately 70°) and the Na^+ cations achieve six-co-ordination in a pentagonal-pyramidal arrangement with the Cl atom in the apical position. The apical position in the six-co-ordination of the Na atom of the cation in compound **4** is directly occupied by the chloride ligand bound to the monovalent gold in the mixed-valence anion $[\{Cl_2Au(\mu\text{-}SAuCl)\}_2]^{2-}$. The Na–Cl distances in **3** and **4** [2.74(3) and 2.659(5) Å, respectively] are close to the sum of the ionic radii, as was the case for the corresponding values in **2**. The packing of compound **4** is shown in Fig. 4(*b*).

Possible Explanation for the Formation of the Compounds.—The general characteristics of the reactions with 15-crown-5-$Na(SBu^t)$ can be summarized as follows. Anionic thiochloroaurates are stabilized in solution in the presence of 15-crown-5, a specific crown ether for the sodium cation; the AuCl group from [AuCl(CO)] survives in all the products obtained by recrystallization from dichloromethane solutions, as a part of a Cl–Au–S arrangement or in the anion $[AuCl_2]^-$. The products obtained depend on the molar ratio Au:S; when it is 1:1 they are $[AuCl_2]^-$ and $[(AuCl)_3SBu^t]^-$, and no disproportionation pathway for Au^I is observed. In an attempt to reproduce independently the synthesis of compound **1** we used the molar ratio $[AuCl(CO)]:[Na(15\text{-crown-}5)][SBu^t]$ of 3:1. Under these conditions the crystalline products **2**–**4** were obtained.

The mixed-valence Au^I–Au^{III} anions contained in compounds **3** and **4** may be formed through the decomposition of the trinuclear $[(AuCl)_3SBu^t]^-$ anion of **1** to the $[Au_4Cl_6S_2]^{2-}$ anion by the redox reaction (3). Our findings are to be

$$2[(AuCl)_3SR]^- \longrightarrow [Au_4Cl_6S_2]^{2-} + R_2 + 2Au \quad (3)$$

compared with the work of Wang and Fackler[7] who were able to synthesize the pure gold(III) compound $[Cl_2Au(\mu\text{-}SPh)_2AuCl_2]$ from $[AuCl(CO)]$ and PhSSPh using analogous experimental conditions, namely $[AuCl(CO)]$ in CH_2Cl_2 under a nitrogen atmosphere. In the same paper, the synthesis of $[\{Au(PPh_3)\}_2SCH_2Ph]^+NO_3^-$ from $[Au(PPh_3)]NO_3$ and $(PhCH_2S)_2$ [or $Na(SCH_2Ph)$] is described.

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