Gold Complexes with Heterocyclic Thiones as Ligands. *X*-Ray Structure Determination of $[Au(C_5H_5NS)_2]ClO_4$*

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Displacement of the weakly co-ordinating tetrahydrothiophene (tht) ligand in [AuX(tht)], $[Au(tht)_2]ClO_4$, or $[Au(PPh_3)(tht)]ClO_4$ (X = Cl or C_6F_5) by heterocyclic thiones HL (HL = $C_3H_5NS_2$, $C_4H_4N_2S$, C_5H_5NS, $C_7H_5NS_2$, or $C_7H_6N_2S$), leads to the formation of neutral or cationic complexes of the types [AuX(HL)], $[Au(HL)_2]ClO_4$, or $[Au(PPh_3)(HL)]ClO_4$. For gold(III) complexes the tht ligand cannot be displaced but $[Au(C_6F_5)_3(OEt_2)]$ reacts with HL to give neutral complexes $[AuR_3(HL)]$. Deprotonation of the NH unit in the cationic complexes leads to neutral monomeric complexes and since the deprotonated N atom is now a donor, binuclear complexes can be prepared by displacement of a weakly co-ordinating ligand from other suitable complexes. The structure of $[Au(HL)_2]ClO_4$ (HL = C_5H_5NS) has been established by *X*-ray crystallography [space group $P\bar{1}$, $a = 9.609(3)$, $b = 15.024(6)$, $c = 16.712(7)$ Å, $\alpha = 97.52(4)$, $\beta = 104.17(2)$, $\gamma = 104.76(2)°$, and $R' = 0.045$ for 5 499 unique observed reflections]. The cations are arranged in a way that is unprecedented for gold(I) compounds. Five of the six cations in the cell are linked by short Au • • • Au contacts (3.3 Å) and the sixth cation is monomeric.

Herein we describe the preparation and properties of gold(I) and gold(III) complexes with heterocyclic ligands (HL) containing the –NH–C=S unit [or $-N{=}C{-}S^-$ for the corresponding anionic ligand L^- formed by deprotonation], with an exocyclic S atom [HL = 1,3-thiazolidine-2-thione ($C_3H_5NS_2$), 1*H*-pyrimidine-2-thione ($C_4H_4N_2S$), pyridine-2-thione (C_5H_5NS), benzo-thiazolidine-2-thione ($C_7H_5NS_2$), or benzimidazole-2-thione ($C_7H_6N_2S$)].

No gold complex containing these ligands has been reported previously.

Results and Discussion

(*a*) *Neutral Gold*(I) *Complexes*.—The tetrahydrothiophene (tht) ligand in gold(I) complexes [AuX(tht)] can readily be displaced by a heterocyclic thione to give neutral complexes of the type [AuX(HL)] [equation (1); X = Cl; HL = $C_4H_4N_2S$

$$[AuX(tht)] + HL \longrightarrow \underset{(\mathbf{1})-(\mathbf{7})}{[AuX(HL)]} + tht \qquad (1)$$

(**1**) or C_5H_5NS (**2**); X = C_6F_5; HL = $C_3H_5NS_2$ (**3**), $C_4H_4N_2S$ (**4**), C_5H_5NS (**5**), $C_7H_5NS_2$ (**6**), or $C_7H_6N_2S$ (**7**)] which can be isolated as white [(**1**), (**3**), and (**6**)], yellow [(**2**), (**5**), and (**7**)], or red [(**4**)] air- and moisture-stable solids, at room temperature. Their acetone solutions are non-conducting but the complexes are only slightly soluble in non-donor organic solvents; only the molecular weight of (**7**) ($CHCl_3$ solution, isopiestic method: *M* 470, calc. 570) has been measured, confirming its monomeric nature.

The i.r. spectra of the complexes show absorptions at ≈3 300 [ν(NH)] and 1 620 [δ(NH)] cm^{-1}. Since no band in the 2 500 [ν(SH)] cm^{-1} region can be observed, the ligands are *S*-bonded to the gold atoms in all complexes (**1**)—(**7**). The ν(Au–Cl) vibration appears at 330s and 322s cm^{-1} in the spectra of complexes (**1**) and (**2**).

(*b*) *Cationic Gold*(I) *Complexes*.—If the starting gold complex is cationic, two different situations can arise depending on whether both or only one of the two ligands bonded to the gold(I) atom are readily displaced. For $[Au(tht)_2]ClO_4$ both ligands are bonded weakly and upon addition of two moles of HL homoleptic cationic complexes are obtained [equation (2);

$$[Au(tht)_2]ClO_4 + 2HL \longrightarrow \underset{(\mathbf{8})-(\mathbf{12})}{[Au(HL)_2]ClO_4} + 2\,tht \qquad (2)$$

HL = $C_3H_5NS_2$ (**8**), $C_4H_4N_2S$ (**9**), C_5H_5NS (**10**), $C_7H_5NS_2$ (**11**), or $C_7H_6N_2S$ (**12**)].

The complexes are white [(**8**), (**11**), and (**12**)] or yellow [(**9**) and (**10**)] solids, which slowly decompose at room temperature. In acetone solution, they are conducting and behave as 1:1 electrolytes. They are insoluble in dichloromethane, n-hexane and diethyl ether. Their i.r. spectra show a strong absorption in the 3 600—3 240 cm^{-1} region due to the ν(N–H) vibration and therefore the two HL ligands are *S*-bonded to the gold atom. Two bands at 1 100s, br and 620m cm^{-1} arise from the ClO_4^- anion.[1]

If the starting gold complex contains only one readily displaceable ligand, mixed cationic complexes are obtained [equation (3); HL = $C_3H_5NS_2$ (**13**), C_5H_5NS (**14**), or $C_7H_5NS_2$ (**15**)].

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* Bis(pyridine-2-thione-*S*)gold(I) perchlorate.

Supplementary data available: H-atom co-ordinates, thermal parameters, and structure factors have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote a full literature citation and the reference number CSD 54694.

$$[Au(PPh_3)(tht)]ClO_4 + HL \longrightarrow [Au(PPh_3)(HL)]ClO_4 + tht \quad (3)$$
$$\textbf{(13)—(15)}$$

The use of $[Au(PPh_3)(OClO_3)]$ as the precursor leads to the same results, but this method is less convenient since the instability of the perchlorato complex leads to impure products. Complexes (**13**)—(**15**) are isolated as white solids, which are 1:1 electrolytes in acetone solution. The HL ligand is again *S*-bonded, as confirmed by a strong band [ν(N–H)] at ≈3 200 cm^{-1} in the i.r. spectra.

(*c*) *Gold*(III) *Complexes.*—Since tht is more strongly bonded to Au^{III} than to Au^{I}, the reactions between $[Au(C_6F_5)_3(tht)]$ and thione ligands lead to equilibria. Therefore, we have used $[Au(C_6F_5)_3(OEt_2)]$ as the starting gold(III) complex with satisfactory results [equation (4); HL = $C_3H_5NS_2$ (**16**), $C_4H_4N_2S$ (**17**), C_5H_5NS (**18**), $C_7H_5NS_2$ (**19**), or $C_7H_6N_2S$ (**20**)].

$$[Au(C_6F_5)_3(OEt_2)] + HL \longrightarrow [Au(C_6F_5)_3(HL)] + Et_2O \quad (4)$$
$$\textbf{(16)—(20)}$$

Complex (**17**) is a red solid, whilst all the other complexes are white solids. They are all air- and moisture-stable, their acetone solutions are non-conducting, and their molecular weights confirm their monomeric nature [complexes (**19**) and (**21**) could not be measured owing to poor solubility]. Their i.r. spectra show bands in the region 3 500—3 200 cm^{-1} assigned to the ν(N–H) vibration; the HL ligands are therefore *S*-bonded. Moreover, two bands at ≈800s and 785s (br) cm^{-1} are indicative of the presence of three C_6F_5 groups.[2]

(*d*) *Deprotonation Reactions of the* NH *Moiety with* Na_2CO_3:*Mono-, Di-, and Poly-nuclear Complexes.*—A set of different processes has been studied.

(*i*) Complexes (**13**)—(**15**) react with solid Na_2CO_3 (excess) to give neutral derivatives [equation (5); L = $C_3H_4NS_2$ (**21**), C_5H_4NS (**22**), or $C_7H_4NS_2$ (**23**)] and the same complexes [and others that are not accessible by the process represented in equation (5)] can be obtained by the reaction [equation (6); L = $C_4H_3N_2S$ (**24**) or $C_7H_5N_2S$ (**25**)] of $[AuCl(PPh_3)]$ with the deprotonated ligand L^- (obtained by treating HL with KOH in methanol).

$$[Au(PPh_3)(HL)]ClO_4 + Na_2CO_3 \longrightarrow NaClO_4 + NaHCO_3 + [AuL(PPh_3)] \quad (5)$$
$$\textbf{(21)—(23)}$$

$$[AuCl(PPh_3)] + KL \longrightarrow [AuL(PPh_3)] + KCl \quad (6)$$
$$\textbf{(21), (23)—(25)}$$

Complexes (**21**)—(**25**) are air- and moisture-stable white solids. Their acetone solutions are non-conducting and they are monomeric in chloroform solution. The i.r. spectra of the complexes do not show bands due to either ClO_4 or to ν(N–H).

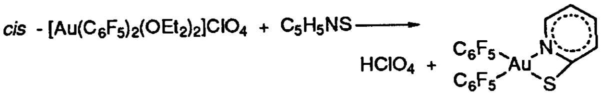
(*ii*) The deprotonated N atom is a potential donor and binuclear complexes can now be obtained [equation (7); L = $C_3H_4NS_2$ (**26**) or C_5H_4NS (**27**)] by reaction with $[Au(C_6F_5)(tht)]$. Binuclear complexes can also be obtained in one-step processes by suitable selection of the reagents in 1:1 mixtures. Thus, for instance, addition of solid Na_2CO_3 to a 1:1 mixture of complex (**5**) and $[NBu_4][AuBr(C_6F_5)]$ gives [equation (8)] the yellow binuclear cationic complex (**28**) which behaves as a 1:1 electrolyte in acetone solution. A mixture of complex (**18**) and $[NBu_4][AuBr(C_6F_5)]$ or $[AuCl(PPh_3)]$ gives, upon deprotonation with solid Na_2CO_3, the anionic complex $[NBu_4][(C_6F_5)_3Au(C_5H_4NS)Au(C_6F_5)]$ (**29**) or the neutral complex $[(C_6F_5)_3Au(C_5H_4NS)Au(PPh_3)]$ (**30**) respectively. The latter can also be prepared by the 1:1 reaction of complex (**14**) with $[NBu_4][AuBr(C_6F_5)_3]$ in the presence of Na_2CO_3. In the i.r. spectra of all these white binuclear complexes ν(N–H) vibrations are absent as expected.

$$[AuL(PPh_3)] + [Au(C_6F_5)(tht)] \longrightarrow [(C_6F_5)AuLAu(PPh_3)] \quad (7)$$
$$\textbf{(26), (27)}$$

$$\underset{\textbf{(5)}}{[Au(C_6F_5)(C_5H_5NS)]} + [NBu_4][AuBr(C_6F_5)] + Na_2CO_3 \longrightarrow [NBu_4][(C_6F_5)Au(C_5H_4NS)Au(C_6F_5)] + NaBr + NaHCO_3 \quad (8)$$

(*iii*) Reaction of complex (**2**) with Na_2CO_3 causes deprotonation of the NH moiety, simultaneous elimination of the Cl^- ligand and precipitation of an insoluble yellow solid of the stoicheiometry $Au(C_5H_4NS)$ (**31**) which is probably polymeric in nature. Both ν(N–H) and ν(Au–Cl) are absent in its i.r. spectrum.

(*iv*) The two OEt_2 ligands in *cis*-$[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ can be readily displaced by pyridine-2-thione with deprotonation of the ligand [equation (9)] and formation of a neutral monomeric auracycle (**32**). Lack of solubility precluded the determination of the molecular weight. The presence of two bands at 800s and 780s cm^{-1} in the i.r. spectrum confirms the *cis* disposition of the C_6F_5 groups.[3]



(9)

(**32**)

(*e*) X-*Ray Crystal Structure of Complex* (**10**).—The asymmetric unit of complex (**10**) consists of three formula units with two entire and two half cations in the asymmetric unit. As expected, the co-ordination geometry at gold is linear [maximum deviation 5.7° at Au(1)]; the Au–S bond lengths (2.28—2.29 Å) lie in the expected range. The cations are arranged in a way that is unprecedented for gold(I) compounds. Five of the six cations in the cell are linked by short Au ··· Au contacts[4] of *ca.* 3.3 Å to form an approximately linear chain, the central gold atom Au(3) lying on a crystallographic symmetry centre (Figure 1). The Au_5 chains in adjacent unit cells are not collinear. The Au(2)–Au(1)–Au(1″) angle is 145.4° and the Au(1) ··· Au(1″) distance is >4.5 Å. The sixth cation is monomeric, its gold atom Au(4) also occupying a symmetry centre.

The protonated nitrogen atoms of the heterocyclic rings form hydrogen bonds to the perchlorate anions [N(112) ··· O(33) (*x*, *y*, 1 + *z*) 2.95, N(122) ··· O(31) (1 − *x*, 1 − *y*, 1 − *z*) 2.87, N(222) ··· O(11) (1 − *x*, 1 − *y*, 1 − *z*) 2.80, and N(42) ··· O(13) 2.97 Å]. A stereographic packing plot is shown in Figure 2.

Experimental

Instrumentation and general experimental techniques were as described earlier.[2] N.m.r. spectra were recorded on a Varian XL

200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external, ^{31}P) and $CFCl_3$ (external, ^{19}F). The yields, C, H, and N analyses, molecular weights and conductivities of the new complexes are listed in Table 1. All the reactions were performed at room temperature.

Preparation of the Complexes.—[AuX(HL)] [X = Cl, HL = $C_4H_4N_2S$ (**1**) *or* C_5H_5NS (**2**); X = C_6F_5, HL = $C_3H_5NS_2$ (**3**), $C_4H_4N_2S$ (**4**), C_5H_5NS (**5**), $C_7H_5NS_2$ (**6**), *or* $C_7H_6N_2S$ (**7**)]. To a solution of [AuCl(tht)][5] (0.256 g, 0.8 mmol) or [Au(C_6F_5)(tht)][5] (0.36 g, 0.8 mmol) in dichloromethane (20 cm^3) was added HL [0.8 mmol, HL = $C_3H_5NS_2$ (0.095), $C_4H_4N_2S$ (0.090), C_5H_5NS (0.089), $C_7H_5NS_2$ (0.134), or $C_7H_6N_2S$ (0.120 g)] and the mixture was stirred for 1 h. The solution was concentrated to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) gave complexes (**1**)—(**7**) [complexes (**1**), (**4**), and (**6**) precipitated from the dichloromethane solution]. N.m.r.: (**1**), δ_H 8.83 [d, *J*(HH) = 5.2 Hz, 2 H] and 7.53 (t, 1 H); (**2**), δ_H 16.4 (1 H, NH), 8.38 (d, 1 H, H^6), 8.07 (ddd, 1 H, H^4), 7.98 (dd, 1 H, H^3), and 7.48 (dt, 1 H, H^5); (**3**), δ_H 8.2 (1 H, NH), 4.2 [t, *J*(HH) 8.0 Hz, 2 H], and 3.2 (t, 2 H); δ_F −117.4 (m, *o*-F), −160.28 [t, *J*(FF) 19.5 Hz, *p*-F], and −163.3 p.p.m. (m, *m*-F); (**5**), δ_H 7.27 (m); δ_F −117.6 (m, *o*-F), −160.4 [t, *J*(FF) 20.0 Hz, *p*-F], and −163.7 p.p.m. (m, *m*-F); (**6**), δ_H 7.66 (m, 1 H), 7.63 (m, 1 H), and 7.53 (m, 2 H); δ_F −117.7 (m, *o*-F), −160.5 [t, *J*(FF) 19.8 Hz, *p*-F], and −163.5 p.p.m. (m, *m*-F); (**7**), δ_H 7.27 (m); δ_F −117.6 (m, *o*-F), −160.4 [t, *J*(FF) 20.1 Hz, *p*-F], and −163.7 p.p.m. (m, *m*-F).

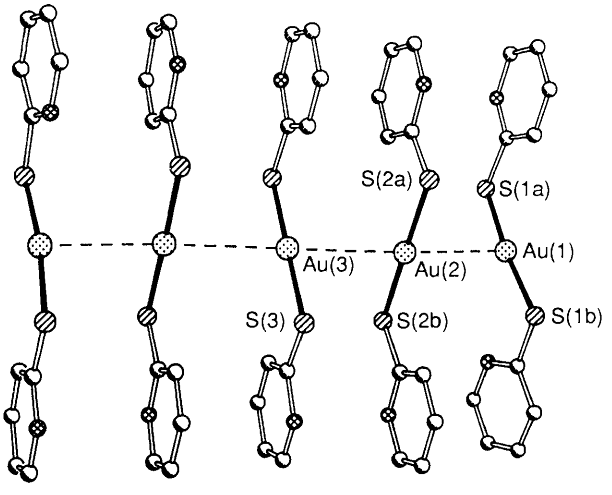


Figure 1. The pentameric cation of complex (**10**) in the crystal. Radii are arbitrary; H atoms omitted for clarity

[Au(HL)$_2$]ClO_4 [HL = $C_3H_5NS_2$ (**8**), $C_4H_4N_2S$ (**9**), C_5H_5NS (**10**), $C_7H_5NS_2$ (**11**), or $C_7H_6N_2S$ (**12**)]. To a solution or suspension of [Au(tht)$_2$]ClO_4 {obtained by a 1 : 1 reaction of [AuCl(tht)][5] and [Ag($OClO_3$)(tht)] in dichloromethane} (0.378 g, 0.8 mmol) in acetone (20 cm^3) was added HL [0.8 mmol, HL = $C_3H_5NS_2$ (0.095), $C_4H_4N_2S$ (0.090), C_5H_5NS (0.089), $C_7H_5NS_2$ (0.134), or $C_7H_6N_2S$ (0.120 g)] and the mixture stirred for 30 min. Evaporation of the solution to *ca.* 5 cm^3 gave (**8**), (**9**), or (**12**) as solids. To obtain complex (**10**) or (**11**) it was necessary to add diethyl ether (15 cm^3). N.m.r.: (**8**), δ_H 7.28 (NH), 3.90 [t, *J*(HH) 7.8 Hz, 2 H], and 3.60 (t, 2 H); (**9**), δ_H 8.90 [d, *J*(HH) 4.9 Hz, 2 H] and 7.6 (t, 1 H); (**10**), 8.46 [d, *J*(HH) 6.2 Hz, 2 H, H^6], 8.12 (m, 4 H, H^3 and H^4), and 7.56 [dt, *J*(HH) 13.0 and 1.6 Hz, 2 H, H^5] [$(CD_3)_2CO$ solution]; (**11**), δ_H 7.8 (m).

[Au(PPh_3)(HL)]ClO_4 [HL = $C_3H_5NS_2$ (**13**), C_5H_5NS (**14**), *or* $C_7H_5NS_2$ (**15**)]. To a solution of [Au(PPh_3)(tht)]ClO_4 {obtained by 1 : 1 reaction of [AuCl(PPh_3)][5] and [Ag($OClO_3$)(tht)] in dichloromethane} (0.517 g, 0.8 mmol) in dichloromethane (20 cm^3) was added HL [0.8 mmol, HL = $C_3H_5NS_2$ (0.095), C_5H_5NS (0.089), or $C_7H_5NS_2$ (0.134 g)] and the mixture stirred for 1 h. Partial concentration of the solution to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) led to precipitation of complexes (**13**)—(**15**). N.m.r.: (**13**), δ_H 7.54 (m, 15 H, PPh_3), 4.37 [t, *J*(HH) 8.3 Hz, 2 H], and 3.69 (t, 2 H); δ_P 37.18 p.p.m. (s);

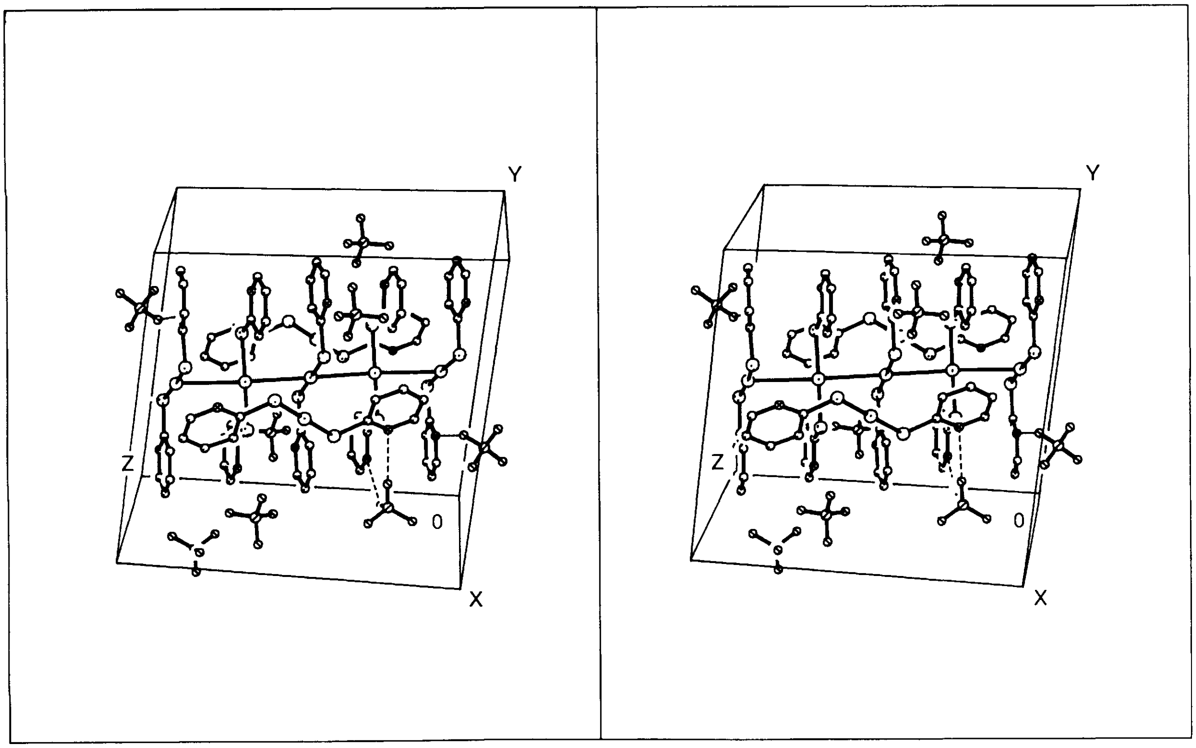


Figure 2. Stereographic packing diagram of complex (**10**). Hydrogen bonds are indicated by dashed lines

Table 1. Analytical data for complexes (**1**)—(**32**)

Complex	Yield (%)	Found (calc.) (%)				*M* Found (calc.)	M.p./°C
		C	H	N	Λ_M*		
(**1**) $[AuCl(C_4H_4N_2S)]$	89	13.8 (13.95)	1.15 (1.15)	8.4 (8.15)	1	—	215
(**2**) $[AuCl(C_5H_5NS)]$	98	17.55 (17.5)	1.45 (1.45)	3.75 (4.05)	3	—	145
(**3**) $[Au(C_6F_5)(C_3H_5NS_2)]$	91	22.1 (22.35)	0.9 (1.05)	2.75 (2.9)	6	—	141
(**4**) $[Au(C_6F_5)(C_4H_4N_2S)]$	67	24.85 (25.2)	0.70 (0.85)	5.85 (5.9)	0	—	194
(**5**) $[Au(C_6F_5)(C_5H_5NS)]$	90	27.4 (27.8)	1.05 (1.05)	2.75 (2.95)	6	—	185
(**6**) $[Au(C_6F_5)(C_7H_5NS_2)]$	85	29.6 (29.4)	0.85 (0.95)	2.65 (2.65)	1	—	267
(**7**) $[Au(C_6F_5)(C_7H_6N_2S)]$	91	30.3 (30.35)	1.15 (1.2)	5.6 (5.45)	3	470 (514)	236
(**8**) $[Au(C_3H_5NS_2)_2]ClO_4$	89	13.85 (13.5)	1.8 (1.9)	5.3 (5.25)	105	—	177
(**9**) $[Au(C_4H_4N_2S)_2]ClO_4$	98	18.65 (18.45)	1.75 (1.55)	10.45 (10.75)	150	—	178
(**10**) $[Au(C_5H_5NS)_2]ClO_4$	97	23.1 (23.15)	1.95 (1.95)	5.55 (5.4)	136	—	172
(**11**) $[Au(C_7H_5NS_2)_2]ClO_4$	95	26.3 (26.65)	1.5 (1.6)	4.3 (4.45)	115	—	126
(**12**) $[Au(C_7H_6N_2S)_2]ClO_4$	70	27.95 (28.2)	1.75 (2.05)	9.1 (9.4)	134	—	225
(**13**) $[Au(PPh_3)(C_3H_5NS_2)]ClO_4$	83	37.55 (37.2)	3.15 (2.95)	2.25 (2.05)	157	—	118
(**14**) $[Au(PPh_3)(C_5H_5NS)]ClO_4$	89	40.95 (41.25)	3.2 (3.0)	1.8 (2.1)	129	—	72
(**15**) $[Au(PPh_3)(C_7H_5NS_2)]ClO_4$	81	40.95 (41.35)	2.75 (2.8)	1.65 (1.95)	137	—	120
(**16**) $[Au(C_6F_5)_3(C_3H_5NS_2)]$	90	30.6 (30.85)	0.65 (0.6)	1.7 (1.7)	2	802 (817)	148
(**17**) $[Au(C_6F_5)_3(C_4H_4N_2S)]$	73	32.2 (32.6)	0.95 (0.5)	3.9 (3.45)	2	—	210
(**18**) $[Au(C_6F_5)_3(C_5H_5NS)]$	87	34.3 (34.15)	0.5 (0.6)	1.55 (1.75)	3	820 (809)	175
(**19**) $[Au(C_6F_5)_3(C_7H_5NS_2)]$	93	34.7 (34.7)	1.1 (0.6)	1.5 (1.6)	2	—	241
(**20**) $[Au(C_6F_5)_3(C_7H_6N_2S)]$	67	35.55 (35.4)	0.75 (0.7)	3.25 (3.3)	1	826 (848)	236
(**21**) $[Au(C_3H_4NS_2)(PPh_3)]$	88	43.35 (43.7)	3.45 (3.3)	2.3 (2.45)	4	582 (577)	159
(**22**) $[Au(C_5H_4NS)(PPh_3)]$	43	48.2 (48.5)	3.15 (3.35)	2.45 (2.45)	10	624 (569)	210
(**23**) $[Au(C_7H_4NS_2)(PPh_3)]$	92	48.0 (48.0)	2.95 (3.05)	2.0 (2.25)	14	582 (625)	167
(**24**) $[Au(C_4H_3N_2S)(PPh_3)]$	90	45.9 (46.35)	3.15 (3.2)	4.8 (4.9)	1	572 (570)	215
(**25**) $[Au(C_7H_5N_2S)(PPh_3)]$	91	49.3 (49.35)	3.45 (3.3)	4.55 (4.6)	1	593 (608)	215
(**26**) $[(C_6F_5)Au(C_3H_4NS_2)Au(PPh_3)]$	80	34.7 (34.45)	2.05 (2.05)	2.05 (1.5)	3	922 (941)	195
(**27**) $[(C_6F_5)Au(C_5H_4NS)Au(PPh_3)]$	73	37.2 (37.3)	2.1 (2.05)	1.6 (1.5)	2	906 (933)	143
(**28**) $[NBu_4][(C_6F_5)Au(C_5H_4NS)Au(C_6F_5)]$	60	36.15 (36.5)	3.4 (3.75)	2.2 (2.6)	178	—	175
(**29**) $[NBu_4][(C_6F_5)_3Au(C_5H_4NS)Au(C_6F_5)]$	75	38.65 (38.2)	3.5 (2.85)	2.05 (2.0)	150	—	170
(**30**) $[(C_6F_5)_3Au(C_5H_4NS)Au(PPh_3)]$	65	38.0 (38.85)	1.8 (1.5)	1.05 (1.1)	1	—	165
(**31**) $[\{Au(C_5H_4NS)\}_n]$	84	19.25 (19.55)	1.25 (1.3)	4.15 (4.55)	1	—	135
(**32**) *cis*-$[Au(C_6F_5)_2(C_5H_4NS)]$	95	31.6 (31.85)	0.65 (0.65)	2.15 (2.2)	3	—	220

* In acetone, S cm^2 mol^{-1}.

Table 2. Atomic co-ordinates (× 10^4) for complex (**10**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	9 282.6(5)	5 716.2(3)	8 896.7(3)	Au(3)	5 000	5 000	5 000
S(1a)	7 496(3)	4 702(2)	9 301(2)	S(3)	6 797(3)	6 118(2)	4 694(2)
C(111)	7 829(10)	3 628(7)	9 113(6)	C(31)	6 409(10)	7 158(6)	4 925(6)
N(112)	6 863(9)	2 896(5)	9 251(5)	N(32)	7 367(9)	7 953(5)	4 807(5)
C(113)	6 974(13)	2 008(8)	9 123(7)	C(33)	7 165(11)	8 816(7)	4 992(6)
C(114)	8 112(14)	1 828(8)	8 846(8)	C(34)	6 042(12)	8 930(8)	5 289(7)
C(115)	9 108(12)	2 568(9)	8 715(7)	C(35)	5 070(11)	8 145(8)	5 403(7)
C(116)	9 004(10)	3 460(8)	8 835(6)	C(36)	5 246(9)	7 269(6)	5 236(6)
S(1b)	11 233(3)	6 725(2)	8 614(2)	Au(4)	10 000	5 000	5 000
C(121)	11 067(10)	7 838(7)	8 828(6)	S(4)	7 895(3)	3 929(2)	4 090(2)
N(122)	9 855(9)	7 985(6)	9 029(5)	C(41)	7 463(9)	4 359(7)	3 180(6)
C(123)	9 685(13)	8 851(8)	9 172(7)	N(42)	6 291(8)	3 797(6)	2 542(5)
C(124)	10 753(13)	9 614(9)	9 129(8)	C(43)	5 814(13)	4 044(9)	1 827(9)
C(125)	12 000(15)	9 484(9)	8 945(8)	C(44)	6 520(12)	4 855(10)	1 663(8)
C(126)	12 185(12)	8 614(8)	8 796(8)	C(45)	7 712(12)	5 460(8)	2 295(8)
Au(2)	7 393.5(4)	5 379.6(3)	6 902.1(3)	C(46)	8 220(10)	5 228(7)	3 057(7)
S(2a)	7 711(3)	3 920(2)	6 642(2)	Cl(1)	4 577(3)	797(2)	2 192(2)
C(211)	6 300(10)	3 157(7)	6 898(6)	O(11)	3 277(8)	479(6)	2 385(8)
N(212)	6 309(8)	2 260(6)	6 810(5)	O(12)	4 426(13)	349(8)	1 423(6)
C(213)	5 312(11)	1 573(7)	6 997(7)	O(13)	5 133(13)	1 723(5)	2 306(9)
C(214)	4 212(12)	1 747(7)	7 271(7)	O(14)	5 602(11)	529(9)	2 727(13)
C(215)	4 125(11)	2 661(8)	7 379(7)	Cl(2)	655(3)	8 400(2)	3 960(2)
C(216)	5 147(10)	3 373(7)	7 202(6)	O(21)	−29(8)	9 060(5)	4 147(8)
S(2b)	7 107(3)	6 843(2)	7 186(2)	O(22)	−73(12)	7 556(5)	4 085(9)
C(221)	8 534(9)	7 629(7)	6 939(6)	O(23)	2 090(8)	8 675(9)	4 436(9)
N(222)	8 514(8)	8 530(5)	7 037(5)	O(24)	736(17)	8 341(12)	3 173(9)
C(223)	9 558(11)	9 220(7)	6 896(7)	Cl(3)	3 128(3)	2 518(2)	−387(2)
C(224)	10 644(12)	9 022(7)	6 581(7)	O(31)	2 501(8)	2 726(8)	239(6)
C(225)	10 689(10)	8 105(7)	6 460(7)	O(32)	3 662(13)	3 282(6)	−667(9)
C(226)	9 644(9)	7 409(7)	6 620(6)	O(33)	4 312(9)	2 204(11)	−75(8)
				O(34)	2 142(13)	1 825(8)	−1 010(9)

Table 3. Bond lengths (Å) for complex (**10**)

Au(1)–S(1a)	2.288(3)	Au(1)–S(1b)	2.282(3)
Au(1)–Au(2)	3.285(1)	S(1a)–C(111)	1.727(11)
C(111)–N(112)	1.331(12)	C(111)–C(116)	1.388(16)
N(112)–C(113)	1.359(14)	C(113)–C(114)	1.359(20)
C(114)–C(115)	1.351(17)	C(115)–C(116)	1.362(18)
S(1b)–C(121)	1.719(11)	C(121)–N(122)	1.349(14)
C(121)–C(126)	1.387(14)	N(122)–C(123)	1.350(16)
C(123)–C(124)	1.353(16)	C(124)–C(125)	1.362(21)
C(125)–C(126)	1.363(19)	Au(2)–S(2a)	2.291(3)
Au(2)–S(2b)	2.288(3)	Au(2)–Au(3)	3.316(1)
S(2a)–C(211)	1.719(10)	C(211)–N(212)	1.340(13)
C(211)–C(216)	1.416(15)	N(212)–C(213)	1.344(13)
C(213)–C(214)	1.319(18)	C(214)–C(215)	1.389(17)
C(215)–C(216)	1.374(15)	S(2b)–C(221)	1.739(10)
C(221)–N(222)	1.348(13)	C(221)–C(226)	1.394(14)
N(222)–C(223)	1.337(13)	C(223)–C(224)	1.356(18)
C(224)–C(225)	1.380(16)	C(225)–C(226)	1.358(14)
Au(3)–S(3)	2.290(3)	S(3)–C(31)	1.714(10)
C(31)–N(32)	1.379(12)	C(31)–C(36)	1.380(14)
N(32)–C(33)	1.366(14)	C(33)–C(34)	1.331(18)
C(34)–C(35)	1.373(16)	C(35)–C(36)	1.370(16)
Au(4)–S(4)	2.278(2)	S(4)–C(41)	1.727(11)
C(41)–N(42)	1.346(10)	C(41)–C(46)	1.392(14)
N(42)–C(43)	1.308(17)	C(43)–C(44)	1.332(19)
C(44)–C(45)	1.371(14)	C(45)–C(46)	1.372(18)
Cl(1)–O(11)	1.351(10)	Cl(1)–O(12)	1.326(11)
Cl(1)–O(13)	1.327(7)	Cl(1)–O(14)	1.341(15)
Cl(2)–O(21)	1.365(10)	Cl(2)–O(22)	1.352(10)
Cl(2)–O(23)	1.339(8)	Cl(2)–O(24)	1.329(16)
Cl(3)–O(31)	1.369(11)	Cl(3)–O(32)	1.325(12)
Cl(3)–O(33)	1.356(13)	Cl(3)–O(34)	1.340(10)

(**14**), δ_H 8.29 [d, *J*(HH) 5.8 Hz, 1 H, H^6], 7.88 (m, 2 H, H^3 and H^4), 7.68 (m, 15 H, PPh_3), and 7.34 [dt, *J*(HH) 5.4 and 1.1 Hz, 1 H, H^5]; δ_P 38.55 p.p.m. (s); (**15**), δ_H 7.6 (m, 15 H, PPh_3) and 7.56 (m, 4 H, $C_7H_5NS_2$); δ_P 36.91 p.p.m. (s).

$[Au(C_6F_5)_3(HL)]$ [HL = $C_3H_5NS_2$ (**16**), $C_4H_4N_2S$ (**17**), C_5H_5NS (**18**), $C_7H_5NS_2$ (**19**), *or* $C_7H_6N_2S$ (**20**)]. To a solution of $[Au(C_6F_5)_3(OEt_2)]$[6] (0.618 g, 0.8 mmol) in dichloromethane (20 cm^3) was added HL [0.8 mmol, HL = $C_3H_5NS_2$ (0.095), $C_4H_4N_2S$ (0.090), C_5H_5NS (0.089), $C_7H_5NS_2$ (0.134), or $C_7H_6N_2S$ (0.120 g)] and the mixture was stirred for 30 min. Evaporation of the solution to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) gave complexes (**16**)—(**20**). N.m.r.: (**16**), δ_H 7.99 (1 H, NH), 4.23 [t, *J*(HH) = 3.87 Hz, 2 H], and 3.71 (t, 2 H); (**19**), δ_H 7.61 (m); δ_F −122.48 (m, *o*-F, C_6F_5 *cis* and *trans*), −157.64 [t, *J*(FF) 20.0 Hz, *p*-F, *cis*-C_6F_5], −157.8 [t, *J*(FF) 20.6 Hz, *trans*-C_6F_5), and −161.93 p.p.m. (m, *m*-F, C_6F_5 *cis* and *trans*); (**20**), δ_H 7.42 (m); δ_F −122.78 (m, *o*-F, C_6F_5 *cis* and *trans*), −158.44 [t, *J*(FF) 19.9 Hz, *p*-F, *trans*-C_6F_5], −158.65 [t, *J*(FF) 20.1 Hz, *p*-F, *cis*-C_6F_5], and −162.39 p.p.m. (m, *m*-F, C_6F_5 *cis* and *trans*).

$[AuL(PPh_3)]$ [L = $C_3H_4NS_2$ (**21**), C_5H_4NS (**22**), $C_7H_4NS_2$ (**23**), $C_4H_3N_2S$ (**24**), *or* $C_7H_5N_2S$ (**25**)]. These complexes can be obtained in two different ways.

(*a*) To a solution of compound (**13**), (**14**), or (**15**) (1 mmol) in dichloromethane (20 cm^3) was added Na_2CO_3 (1 g) and the mixture stirred for 1 h. The excess of Na_2CO_3 was filtered off. The solution was concentrated to *ca.* 2 cm^3 and addition of diethyl ether (20 cm^3) gave complexes (**21**)—(**23**).

(*b*) To a solution of HL [0.8 mmol, HL = $C_3H_5NS_2$ (0.095), $C_4H_4N_2S$ (0.090), $C_7H_5NS_2$ (0.134), or $C_7H_6N_2S$ (0.120 g)] in methanol (20 cm^3) was added a solution of KOH in methanol (14 cm^3, 0.125 mol dm^{-3}) and the mixture was stirred for 30 min; $[AuCl(PPh_3)]$ (0.396 g, 0.8 mmol) was then added and the mixture stirred for 2 h. Concentration to *ca.* 2 cm^3 and addition of n-hexane (20 cm^3) gave (**21**) and (**23**)—(**25**). N.m.r.: (**21**), δ_H 7.55 (m, 15 H, PPh_3), 4.29 [t, *J*(HH) 8.1 Hz, 2 H], and 3.39

Table 4. Bond angles (°) for complex (**10**)

S(1b)–Au(1)–S(1a)	174.3(1)	Au(2)–Au(1)–S(1a)	97.7(1)	C(225)–C(224)–C(223)	118.3(10)	C(226)–C(225)–C(224)	121.2(11)
Au(2)–Au(1)–S(1b)	87.7(1)	C(111)–S(1a)–Au(1)	104.8(4)	C(225)–C(226)–C(221)	119.5(10)	S(3)–Au(3)–Au(2)	87.3(1)
N(112)–C(111)–S(1a)	116.5(8)	C(116)–C(111)–S(1a)	126.1(8)	C(31)–S(3)–Au(3)	105.8(4)	N(32)–C(31)–S(3)	116.9(8)
C(116)–C(111)–N(112)	117.4(10)	C(113)–N(112)–C(111)	123.1(10)	C(36)–C(31)–S(3)	125.6(7)	C(36)–C(31)–N(32)	117.4(9)
C(114)–C(113)–N(112)	120.5(10)	C(115)–C(114)–C(113)	116.9(12)	C(33)–N(32)–C(31)	121.0(9)	C(34)–C(33)–N(32)	122.0(10)
C(116)–C(115)–C(114)	123.3(13)	C(115)–C(116)–C(111)	118.9(10)	C(35)–C(34)–C(33)	117.8(11)	C(36)–C(35)–C(34)	122.0(11)
C(121)–S(1b)–Au(1)	107.5(4)	N(122)–C(121)–S(1b)	121.5(7)	C(35)–C(36)–C(31)	119.8(9)	C(41)–S(4)–Au(4)	107.4(3)
C(126)–C(121)–S(1b)	120.5(9)	C(126)–C(121)–N(122)	118.0(10)	N(42)–C(41)–S(4)	116.4(7)	C(46)–C(41)–S(4)	125.6(6)
C(123)–N(122)–C(121)	122.2(9)	C(124)–C(123)–N(122)	120.5(12)	C(46)–C(41)–N(42)	118.0(9)	C(43)–N(42)–C(41)	122.9(9)
C(125)–C(124)–C(123)	118.3(13)	C(126)–C(125)–C(124)	121.9(12)	C(44)–C(43)–N(42)	121.8(10)	C(45)–C(44)–C(43)	117.7(13)
C(125)–C(126)–C(121)	119.0(12)	S(2a)–Au(2)–Au(1)	90.8(1)	C(46)–C(45)–C(44)	121.8(11)	C(45)–C(46)–C(41)	117.7(8)
S(2b)–Au(2)–Au(1)	88.2(1)	S(2b)–Au(2)–S(2a)	179.0(1)	O(12)–Cl(1)–O(11)	108.8(7)	O(13)–Cl(1)–O(11)	116.3(8)
Au(3)–Au(2)–Au(1)	170.7(1)	Au(3)–Au(2)–S(2a)	92.0(1)	O(13)–Cl(1)–O(12)	113.1(9)	O(14)–Cl(1)–O(11)	105.6(9)
Au(3)–Au(2)–S(2b)	89.1(1)	C(211)–S(2a)–Au(2)	106.6(4)	O(14)–Cl(1)–O(12)	106.8(10)	O(14)–Cl(1)–O(13)	105.4(7)
N(212)–C(211)–S(2a)	116.0(8)	C(216)–C(211)–S(2a)	127.5(8)	O(22)–Cl(2)–O(21)	110.8(7)	O(23)–Cl(2)–O(21)	110.0(7)
C(216)–C(211)–N(212)	116.5(9)	C(213)–N(212)–C(211)	124.1(10)	O(23)–Cl(2)–O(22)	109.9(8)	O(24)–Cl(2)–O(21)	110.3(10)
C(214)–C(213)–N(212)	121.0(11)	C(215)–C(214)–C(213)	118.4(10)	O(24)–Cl(2)–O(22)	111.2(9)	O(24)–Cl(2)–O(23)	104.3(9)
C(216)–C(215)–C(214)	121.3(11)	C(215)–C(216)–C(211)	118.7(10)	O(32)–Cl(3)–O(31)	110.8(8)	O(33)–Cl(3)–O(31)	109.6(7)
C(221)–S(2b)–Au(2)	107.5(4)	N(222)–C(221)–S(2b)	116.0(8)	O(33)–Cl(3)–O(32)	106.6(8)	O(34)–Cl(3)–O(31)	110.9(7)
C(226)–C(221)–S(2b)	126.4(8)	C(226)–C(221)–N(222)	117.5(9)	O(34)–Cl(3)–O(32)	112.0(8)	O(34)–Cl(3)–O(33)	106.7(8)
C(223)–N(222)–C(221)	123.1(9)	C(224)–C(223)–N(222)	120.3(10)				

(t, 2 H); δ_P 38.78 p.p.m. (s); (**22**), δ_P 33.16 p.p.m. (s); (**23**), δ_H 7.75 (m, 2 H), 7.7 (m, 15 H, PPh_3), and 7.35 (m, 2 H); δ_P 38.41 p.p.m. (s); (**24**), δ_H 8.39 [d, *J*(HH) 5.13 Hz, 2 H], 7.50 (m, 15 H, PPh_3), and 6.88 (t, 1 H); δ_P 39.09 p.p.m. (s); (**25**), δ_H 7.6 (m); δ_P 38.04 p.p.m. (s).

$[(C_6F_5)AuLAu(PPh_3)]$ [L = $C_3H_4NS_2$ (**26**) *or* C_5H_4NS (**27**)]. A mixture of (**21**) (0.173 g, 0.3 mmol) or (**22**) (0.171 g, 0.3 mmol) and $[Au(C_6F_5)(tht)]$[5] (0.136 g, 0.3 mmol) in dichloromethane (20 cm^3) was stirred for 2 h. Partial concentration of the solution to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) led to the precipitation of (**26**) or (**27**). N.m.r.: (**27**), δ_P 36.98 p.p.m. (s).

$[NBu_4][(C_6F_5)Au(C_5H_4NS)Au(C_6F_5)]$ (**28**). A mixture of compound (**5**) (0.38 g, 0.8 mmol), $[NBu_4][AuBr(C_6F_5)]$[7] (0.55 g, 0.8 mmol), and Na_2CO_3 (1 g) in dichloromethane (30 cm^3) was stirred for 2 h. The excess of Na_2CO_3 was filtered off. Evaporation of the solution to *ca.* 5 cm^3 gave (**28**) as a yellow solid.

$[NBu_4][(C_6F_5)_3Au(C_5H_4NS)Au(C_6F_5)]$ (**29**). To a suspension of compound (**18**) (0.65 g, 0.8 mmol) and Na_2CO_3 (1 g) in dichloromethane (20 cm^3) was added $[NBu_4][AuBr(C_6F_5)]$[7] (0.55 g, 0.8 mmol) and the mixture was stirred for 2 h. The excesses of Na_2CO_3 and NaBr were filtered off and the solution was evaporated to *ca.* 5 cm^3; addition of n-hexane (10 cm^3) gave complex (**29**).

$[(C_6F_5)_3Au(C_5H_4NS)Au(PPh_3)]$ (**30**). This complex can be obtained in two different ways. (*a*) A mixture of compound (**18**) (0.65 g, 0.8 mmol), $[AuCl(PPh_3)]$ (0.396 g, 0.8 mmol), and Na_2CO_3 (1 g) in dichloromethane (20 cm^3) was stirred for 2 h. The excesses of Na_2CO_3 and NaCl were filtered off and the solution was evaporated to *ca.* 5 cm^3; addition of n-hexane (15 cm^3) gave complex (**30**).

(*b*) A mixture of compound (**14**) (0.536 g, 0.8 mmol), $[NBu_4][AuBr(C_6F_5)_3]$[2] (0.816 g, 0.8 mmol), and Na_2CO_3 (1 g) in dichloromethane (20 cm^3) was stirred for 2 h. The excesses of Na_2CO_3, NaBr, and NBu_4ClO_4 which precipitated were filtered off. Partial concentration of the solution to *ca.* 5 cm^3 and addition of n-hexane (20 cm^3) led to precipitation of (**30**); δ_P 34.28 p.p.m. (s).

$[\{Au(C_5H_4NS)\}_n]$ (**31**). To a solution of compound (**2**) (1.37 g, 4 mmol) in dichloromethane (20 cm^3) was added Na_2CO_3 (1 g). The suspension was stirred for 2 h. The yellow solid (**31**) which precipitated was filtered off and washed with water (5 × 5 cm^3). A second crop was obtained by evaporation of the dichloromethane solution to *ca.* 5 cm^3 and addition of diethyl ether (20 cm^3). Complex (**31**) was recrystallized from dichloromethane–diethyl ether.

cis-$[Au(C_6F_5)_2(C_5H_4NS)]$ (**32**). To a solution of *cis*-$[Au(C_6F_5)_2(OEt_2)_2]ClO_4$[8] (1 mmol) in diethyl ether (20 cm^3) was added C_5H_5NS (0.111 g, 1 mmol) and the mixture was stirred for 20 h. The white solid which precipitated was recrystallized from dichloromethane–hexane.

X-Ray Crystal Structure Determination of Complex (**10**).—*Crystal data.* $C_{10}H_{10}AuClN_2O_4S_2$, M = 517.77, triclinic, space group $P\bar{1}$, a = 9.609(3), b = 15.024(6), c = 16.712(7) Å, α = 97.52(4), β = 104.17(2), γ = 104.76(2)°, U = 2 213.6 Å^3, Z = 6, D_c = 2.33 Mg m^{-3}, $F(000)$ = 1 464, λ(Mo-K_α) = 0.710 69 Å, μ = 10.4 mm^{-1}, T = 293 K. Yellow prism, 0.35 × 0.25 × 0.15 mm.

Data collection and refinement. Intensity measurements were performed on a Stoe-Siemens four-circle diffractometer using monochromated Mo-K_α radiation. Of 7 934 reflections to $2\theta_{max.}$ 50°, 7 791 were unique and 5 499 with $F > 4\sigma(F)$ used for all calculations (program system XS/XLS, written by Professor G. M. Sheldrick). An absorption correction based on ψ scans gave transmission factors of 0.58—0.77. Cell constants were refined from 2θ values of 50 reflections in the range 20—23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined anisotropically to R 0.047, R' 0.045. Hydrogen atoms were included using a riding model. The perchlorate ions were refined with Cl–O bond lengths and O $\cdots$ O non-bonded distances restrained to be equal (σ 0.01, 0.02 Å respectively). The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003F^2$; 545 parameters; S 1.3; max. Δ/σ 0.09; max. $\Delta\rho$ 1 e Å^{-3}. Final atomic co-ordinates are presented in Table 2, with bond lengths and angles in Tables 3 and 4.

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

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