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Synthesis, characterisation and substitution reactions of gold(III) C,N-chelates

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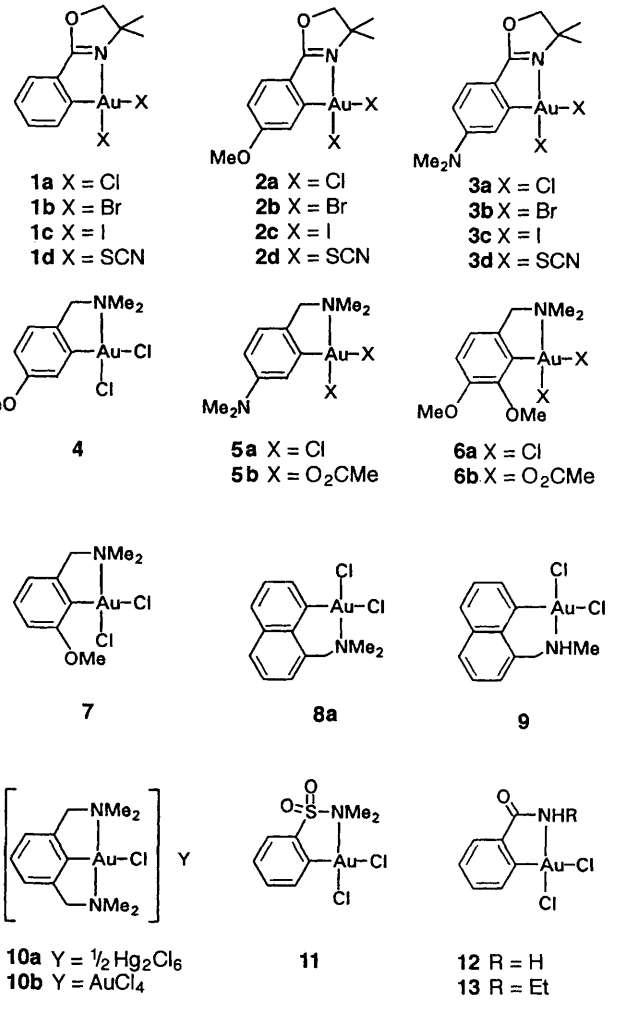
New complexes of the type $[AuCl_2L]$ have been prepared, where L is a chelate consisting of a phenyl group bearing an N-donor substituent (oxazoline and/or dimethylaminomethyl). The structures of two of these, together with that of $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2[Hg_2Cl_6]$, have been determined by X-ray crystallography; the gold atoms exhibit strict square-planar geometry in all cases. The chloride ligands undergo ready substitution by other halides, thiocyanate, acetate or diethyldithiocarbamate. The monodithiocarbamate complexes $[Au(S_2CNEt_2)L]^+$ contain chelated S_2CNEt_2 groups whereas in $[Au(S_2CNEt_2)_2L]$ the L ligand is monodentate (through C), one S_2CNEt_2 is monodentate, the other bidentate; in solution the two S_2CNEt_2 ligands appear equivalent on the NMR time-scale, indicating a rapid equilibrium between the two possible forms.

Following the discovery[1] and exploitation[2] of the antitumour properties of platinum(II) complexes, many new compounds have been synthesised and screened, but the square-planar complexes cisplatin [*cis*-diamminedichloroplatinum(II)] and carboplatin [*cis*-diammine(cyclobutane-1,1-dicarboxylato)-platinum(II)] remain amongst the most successful.[3]

Since gold(III) also usually shows square-planar co-ordination we have established a programme to investigate complexes structurally related to the effective platinum compounds, in the hope that some might show antitumour properties. The formation of neutral complexes with a *cis*-MX_2 configuration is most readily achieved using a mononegative bidentate ligand to occupy the other two co-ordination positions. We have previously reported the synthesis of complexes containing N,O^- ligands,[4] which proved to be unstable under biological conditions. However, more recently we showed that the N,C^--bonded $[AuCl_2(dmamp)]$ [dmamp = 2-(*N*,*N*-dimethylaminomethyl)phenyl] possesses *in vitro* antitumour activity and has *in vivo* activity against the human breast tumour (ZR-75-1) parallel to that of cisplatin.[5] The corresponding diacetato complex $[Au(O_2CMe)_2(dmamp)]$ is more soluble and more active.[6]

We now report the preparation, characterisation and reactions of a variety of new gold(III) complexes containing other mononegative N,C^- ligands together with two containing a mononegative N,C^-,N ligand.



Results

Chelated organogold(III) complexes can readily be prepared by transmetallation from the corresponding organomercury(II) compounds.[7–9] We have used this route with the new arylmercury(II) compounds recently reported by us.[10] Reaction with $[NMe_4][AuCl_4]$ in dry acetone or acetonitrile, in the presence of one molar equivalent of NMe_4Cl, gives the chlorogold(III) complexes **1a**, **2a**, **3a**, **4**, **5a**, **6a** and **7** in fairly good yield, as yellow solids. The function of the NMe_4Cl is to encourage precipitation of $[NMe_4]_2[Hg_2Cl_6]$, shifting the equilibrium in favour of the organogold complex. Complexes **8a**, **9** and the ionic **10a**, containing a $[Hg_2Cl_6]^{2-}$ anion, were obtained similarly, but without adding NMe_4Cl, which appeared to inhibit the reaction. Complex **10b**, containing the $[AuCl_4]^-$ anion, was obtained in aqueous solution; in this medium the mercury remains predominantly as $HgCl_2$ and the anion $[Hg_2Cl_6]^{2-}$ is not formed. The transmetallation reaction appears to be sensitive to the solvent chosen, since arylmercury compounds containing 2-SO_2NMe_2 or 2-$CONH_x$-Et_{2-x} (x = 0–2) substituents showed no reaction in acetone or acetonitrile but gave good reaction in dimethyl sulfoxide (dmso) (NMR evidence; the spectra show that reaction is complete only after several hours). Unfortunately, we have not yet been able to isolate these new gold complexes in good condition from dmso, but the NMR spectra (see below)

indicate that they are analogous to the other products, and we formulate them as **11**–**13**. The reactions of HgR(Cl) [R = 2,5-(*N*,*N*-dimethylaminomethyl)phenyl, 2-(dimethylamino)-6-(*N*,*N*-dimethylaminomethyl)phenyl or 2-methoxy-6-(*N*-methylaminomethyl)phenyl] gave only deposits of gold metal in all solvents tried.

Since the substitution chemistry of gold(III)–dmamp complexes has been well explored,[5,11–14] we have concentrated our efforts on complexes of the oxazoline-substituted ligands. Simple substitution reactions of the chloro-complexes **1a**–**3a** with stoichiometric amounts of alkali-metal salts gave the corresponding bromo- (**1b**–**3b**), iodo- (**1c**–**3c**) or thiocyanato-complexes (**1d**–**3d**). Yields were low, presumably because of the susceptibility of the oxazolinyl group to nucleophilic attack; this group is often used in organic synthesis as a protecting group for carboxylic acids because of the ease with which it can be removed under relatively mild conditions.[15] A similar observation was made during reactions with silver acetate (see below).

It also proved possible to substitute a single chloride ligand in complex **3a** by reaction in dichloromethane with a small amount of dmso in the presence of silver perchlorate. The resulting complex, **3e**, was a 1:1 electrolyte in acetone (96 S mol^{-1}). A similar reaction occurred with 1 molar equivalent of triphenylphosphine to give **1e** and **3f** (the amount of phosphine has to be carefully controlled to avoid side reactions). Other substitution reactions will be described below. Analytical data for all the new materials are given in Table 1.

Spectroscopic properties

The infrared spectra of the compounds (Table 2) are consistent with the presence of the expected ligands. For the chloro-complexes **1a**–**3a**, **4**, **5a**, **6a**, **7**, **8a** and **9** bands are observed at about 350 and 305 cm^{-1} which may be assigned, on the basis of the *trans* influence, to the stretching of Au–Cl bonds *trans* to the nitrogen and carbon atoms of the chelate respectively. For **10a** and **10b** a single gold–chlorine stretching frequency is observed for the organogold cation, at 314 and 307 cm^{-1} respectively; additional bands are present at 360–340 cm^{-1} due to the metal–chlorine vibrations of the inorganic anions. The ν(C–N) bands of **1d**–**3d** suggest that the thiocyanate ligands are S-bonded, as would be expected; the C–S bands were obscured by absorptions due to the organic ligands. Gold–carbon stretching frequencies are observed at 430–440 cm^{-1} for the phenyl compounds, and at 424–429 cm^{-1} for the naphthyl derivatives **8a** and **9**.

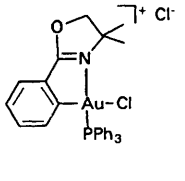
For **1a**–**1c**, **2a**–**2c** and **3a**–**3c** the typical bands of the oxazoline group occur at significantly lower frequencies than for the free aromatics [ν(C–N) 1649–1661, 1585–1612 and 1562–1589 cm^{-1} for the three molecules], indicating that this group is co-ordinated to gold. This is in marked contrast to the corresponding mercury derivatives, HgR(Cl), which are two-co-ordinate and show values very close to those of the free aromatics.[10]

The infrared spectrum of the dmso complex **3e** shows a single Au–Cl stretching frequency at 356 cm^{-1}, consistent with chloride *trans* to nitrogen. Substitution has therefore occurred at the kinetically controlled site, *trans* to carbon. The S–O stretching frequency of the co-ordinated dmso appears at 1186 cm^{-1}, which indicates co-ordination through sulfur.[16] A band at 429 cm^{-1} is more intense than expected for ν(Au–C), and may be ν(Au–S).[17] The triphenylphosphine derivatives **1e** and **3f** also show a single ν(Au–Cl), but at markedly lower frequencies (*ca.* 310 cm^{-1}). This suggests the configuration which is normally found for monosubstitution in this type of system, where the incoming ligand (eventually) occupies the position *trans* to nitrogen. It is generally expected that the two softest ligands will be *cis* to each other in the thermodynamically most stable isomer.

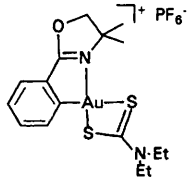
The NMR spectra (Tables 3–5, numbering as in Scheme 1) are very much as expected,[5] and also indicate co-ordination of the oxazoline group: there are strong downfield shifts for C^7 relative to the free aromatics and to the corresponding mercury complexes. The same applies to the CH_2 and CH_3 resonances of the CH_2NMe_2 groups of complexes **4**, **5a**, **6a**, **10a** and **10b**. As we have shown in the case of gold(III)–dmamp complexes, such downfield shifts are diagnostic of co-ordination of the nitrogen atom.[5]

For all the complexes studied, C^1 and, to a lesser extent, C^6 also show strong downfield co-ordination shifts, which mostly increase as X changes from Cl to Br to I (Table 5); C^2 would be expected to show similar shifts but, as for the mercury derivatives,[10] these are masked by the effects of the substituent groups.

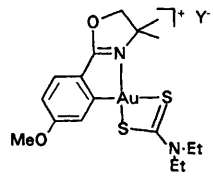
The ^{13}C NMR spectra of solutions in $(CD_3)_2SO$ of HgR(Cl) [R = $C_6H_4SO_2NMe_2$-2 or $C_6H_4C(O)NH_xEt_{2-x}$-2 (x = 1 or 2)] changed dramatically when $Na[AuCl_4]$ was added. New sets of signals appeared rapidly and after some hours were the only peaks in the spectra. The aromatic region then strongly resembled that of the other chelated gold(III) complexes (Table 6). In particular, there were marked downfield shifts for the carbon atoms of the SO_2NMe_2, $C(O)NH_2$ and C(O)NHEt groups, indicating co-ordination of the nitrogen atoms. Thus, although they were not isolated, it is



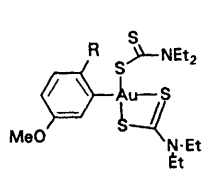
1e



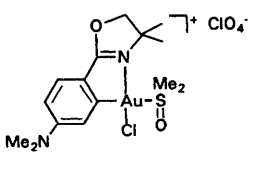
1f



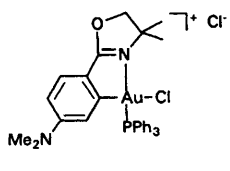
2e Y = BPh_4
2f Y = PF_6



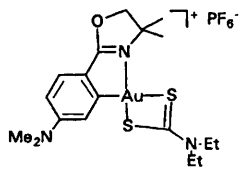
2g R =



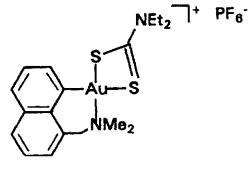
3e



3f



3g



8b

Table 1 Analytical data[a] and yields

Compound	Analysis (%) C	H	N	X[b]	Au	*m/z*	Yield (%)
1a	30.2 (29.9)	2.7 (2.7)	3.2 (3.2)	15.9 (16.1)	44.4 (44.6)		85
1b	24.6 (24.9)	2.3 (2.3)	2.6 (2.6)	30.3 (30.1)			45
1c	21.2 (21.2)	1.7 (1.9)	2.2 (2.2)	40.2 (40.6)			33
1d	32.3 (32.0)	2.4 (2.5)	8.7 (8.6)	13.2 (13.1)			65
1e	49.4 (49.4)	3.8 (3.8)	2.1 (2.0)	4.8 (4.4)			
1f	28.6 (28.9)	3.1 (3.3)	4.2 (4.2)	10.0 (9.6)	29.9 (29.7)		68
2a	30.8 (30.5)	2.9 (3.0)	3.2 (3.0)	14.7 (15.0)	41.5 (41.7)	472	82
2b	25.9 (25.7)	2.5 (2.5)	2.5 (2.5)	28.1 (28.5)			48
2c	22.2 (22.0)	2.0 (2.1)	2.1 (2.1)	38.7 (38.8)			32
2d	32.7 (32.4)	2.3 (2.7)	8.4 (8.1)	12.5 (12.4)			71
2e	56.6 (56.7)	4.8 (5.1)	3.2 (3.2)	7.0 (7.4)			66
2f	29.1 (29.4)	3.5 (3.5)	4.0 (4.0)	9.2 (9.2)			68
2g	38.2 (37.9)	4.9 (4.9)	6.0 (6.0)	18.4 (18.4)			63
3a	32.0 (32.3)	3.2 (3.5)	5.8 (5.8)	14.8 (14.6)	40.5 (40.6)	485	83
3b	27.5 (27.2)	3.0 (3.0)	4.8 (4.9)	28.0 (27.8)			42
3c	23.1 (23.4)	2.4 (2.5)	4.1 (4.2)	38.5 (38.0)			34
3d	34.0 (34.3)	3.2 (3.2)	10.6(10.6)	12.2 (12.1)			67
3e	29.2 (28.7)	3.7 (3.7)	4.5 (4.5)	5.5 (5.1)			
3f	49.5 (49.8)	4.6 (4.3)	3.4 (3.7)	4.1 (4.1)			
3g	30.8 (30.5)	3.8 (3.8)	5.9 (5.9)	9.5 (9.1)			63
4a	27.5 (27.8)	3.3 (3.2)	3.5 (3.2)	16.4 (16.4)	45.6 (45.6)	397[c]	87
5a	29.9 (29.7)	3.8 (3.8)	6.2 (6.3)	15.8 (16.0)	44.2 (44.3)		68
5b	36.9 (36.6)	5.0 (4.7)	5.7 (5.7)				75
6a	28.3 (28.6)	3.4 (3.5)	3.0 (3.0)	15.9 (15.4)	42.4 (42.6)	462[d]	85
6b	35.1 (35.4)	4.6 (4.3)	2.8 (2.7)				73
6c	33.5 (33.7)	3.4 (3.5)	5.4 (5.6)				
7a	27.6 (27.8)	3.1 (3.2)	3.2 (3.2)	16.5 (16.4)	45.8 (45.6)		78
8a	34.8 (34.5)	3.2 (3.1)	3.4 (3.1)	16.2 (15.7)	43.5 (43.6)	402[c]	62
9	32.9 (32.9)	2.7 (2.7)	3.1 (3.2)	16.2 (16.2)	44.1 (45.0)		58
10a	20.0 (19.7)	2.2 (2.6)	3.9 (3.8)	18.8 (19.4)	26.8 (27.0)		83
10b	18.5 (18.9)	2.2 (2.5)	3.4 (3.7)	22.9 (23.3)	50.9 (51.7)	423[e]	79

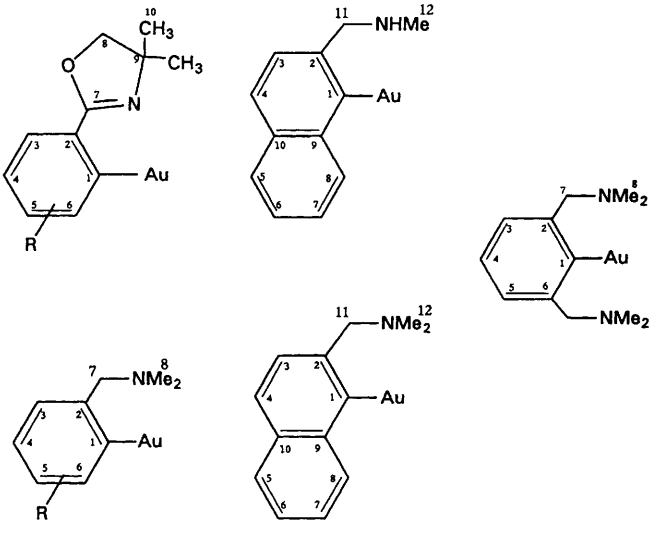
[a] Calculated values in parentheses. [b] Cl, Br, I, P or S as appropriate. [c] $M - Cl$. [d] M^+. [e] $M - AuCl_4$.

Table 2 Selected infrared bands (cm^{-1}) for the gold complexes

Complex	ν(Au–Cl)		ν(Au–C)	ν(C–N)		ν(C–O)	
1a	354	305	431	1620	1576	—	1037
1b				1622	1572	—	1037
1c				1619	1570		1038
1d				1619	1585[a]		
1e		312		1620	1576		
1f				1616	1577		
2a	355	308	437	1607	1585		1028
2b				1609	1589		1035
2c				1611	1585		1030
2d				1605	1589[b]		
2e				1616	1577		
2f				1610	1587		
2g				1643	1585		1035
3a	356	300	440	1597	1529	1365	
3b				1595	1524	1360	
3c				1597	1529	1365	
3d				1597	1538[c]		
3e[d]	356			1599	1585		
3f		310		1593	1515		
3g				1595	1535		
4a	354	303	439	1271		1078	
5a	355	304	435	1340	1020		
6a	354	304	439	1271		1078	
7a	353	303	441	1245		1078	
8a	355	307	424	1074			
9	354	307	429	1078			
10a	351	314	418	1089			
10b	360[e]	307		1093			

[a] 2120, 2075 cm^{-1} for SCN ligand. [b] 2116, 2073 cm^{-1} for SCN ligand. [c] 2117, 2073 cm^{-1} for SCN ligand. [d] Also ClO_4^- at 1091, 623; ν(S=O) 1186; ν(Au–S) 429 cm^{-1}. [e] For $[AuCl_4]^-$.

certain that the chelated dichlorogold(III) complexes **11**–**13** were formed in solution.



Scheme 1

Crystal structures

The structures of the chloro-complexes **1a**, **6a** and **10a** were confirmed by X-ray crystallography. Selected bond distances and angles are given in Tables 7 and 8. Views of the molecular structures are displayed in Figs. 1–3.

In complexes **1a** and **6a** the gold atoms have essentially square-planar $CNCl_2$ co-ordination, and **10a** CN_2Cl, with Au and the four ligand atoms being closely coplanar in each case (mean deviations from the planes: 0.0076, 0.0550 and 0.0071 Å for **1a**, **6a** and **10a**, respectively). The Au–C, Au–N and Au–Cl bond distances are very similar to those reported for other gold(III) complexes.[5,11,12,18] For **1a** and **6a**, the two Au–Cl

Table 3 Proton NMR data (δ, $CDCl_3$ solutions unless otherwise noted)

Complex	R	H^3	H^4	H^5	H^6	H^7	H^8	H^{10}	R
1a		7.4 (d)	7.4 (dd)	7.4 (dd)	7.95 (d)		4.8 (s)	1.75 (s)	
1b		7.35 (d)	7.35 (dd)	7.35 (dd)	8.2 (d)		4.55 (s)	1.8 (s)	
1c		7.4 (d)	7.3 (dd)	7.3 (dd)	8.55 (d)		4.5 (s)	1.85 (s)	
2a	5-OMe	7.3 (d)	6.8 (dd)		7.55 (d)		4.6 (s)	1.8 (s)	3.9 (s)
2b	5-OMe	7.3 (d)	6.75 (dd)		7.8 (d)		4.5 (s)	1.8 (s)	3.85 (s)
2c	5-OMe	7.35 (d)	6.75 (dd)		8.15 (d)		4.45 (s)	1.8 (s)	3.85 (s)
3a	5-NMe_2	7.1 (d)	6.4 (dd)		7.2 (d)		4.5 (s)	1.7 (s)	3.05 (s)
3b	5-NMe_2	7.1 (d)	6.4 (dd)		7.35 (d)		4.45 (s)	1.7 (s)	3.05 (s)
3c	5-NMe_2	7.1 (s)	6.4 (dd)		7.5 (d)		4.45 (s)	1.75 (s)	3.05 (s)
4	5-OMe	7.0 (d)	6.75 (d)		7.0 (s)		4.3 (s)	3.25 (s)	3.75 (s)
5a	5-NMe_2	6.95 (d)	6.6 (d)		7.05 (s)	4.25 (s)	3.2 (s)		3.2 (s)
5b[a]	5-NMe_2	6.8 (d)	6.5 (d)		6.3 (s)	4.1 (s)	2.85 (s)		3.1 (s)
6a	5,6-$(OMe)_2$	6.8 (d)	6.85 (d)			4.3 (s)	3.1 (s)		3.8 (s), 3.85 (s)
8a[b,c]		7.85 (d)	7.95 (dd)	7.5 (d)	7.5 (d)	7.3 (dd)	7.8 (d)		3.3 (s)
10a[b]		7.25 (d)	7.85 (dd)	7.25 (d)		4.95 (s)	3.4 (s)		
10b[b]		7.05 (d)	7.3 (dd)	7.05 (d)		4.85 (s)	3.35 (s)		

[a] For $MeCO_2$ group: δ 2.1 (s) and 1.95 (s). [b] In $(CD_3)_2SO$. [c] For NMe_2, δ 4.9 (s).

Table 4 Carbon-13 NMR data (δ, $CDCl_3$ solutions unless otherwise noted)

Complex	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	R
1a	147.7	126.5	128.5	128.5	135.0	130.6	179.7	84.8	69.0	27.3	
1b	148.7	127.4	127.4	128.8	135.3	132.8	180.5	84.5	69.7	27.9	
1c	150.2	127.8	127.2	128.9	136.3	135.5	182.4	83.5	70.2	28.7	
2a	149.2	117.8	114.7	115.5	163.6	129.9	179.3	84.6	68.6	27.3	56.0
2b	150.2	118.6	114.2	117.9	163.7	130.0	180.0	84.3	68.2	27.8	55.9
2c	151.9	120.6	113.2	122.0	163.9	130.4	182.0	83.6	70.0	29.0	56.0
3a	153.7	110.1	109.9	129.6	149.1	131.0	179.3	84.4	68.0	27.5	40.5
3b	150.4	110.4	109.5	129.6	153.6	152.3	179.5	84.1	68.3	27.7	40.4
3c	150.2	110.8	109.4	130.3	153.6	133.2	179.8	83.9	68.6	27.9	40.3
4	148.6	135.7	115.4	115.8	157.4	123.9	75.6	53.8			55.7
5a	148.5	131.7	113.0	114.6	149.5	124.0	75.5	40.9			53.6
5b[a]	148.5	130.1	112.2	111.7	137.7	122.8	74.6	40.3			52.7
6a	149.0	136.0	112.9	118.5	153.8	153.9	76.2	53.6			56.3, 62.6
10a[b]	162.4	146.8	126.0	133.3	126.0	146.8	81.2	58.1			
10b[b]	162.5	146.9	126.3	133.6	126.3	146.9	81.4	58.2			
11[b]	142.0	146.1	138.5	130.4	136.7	133.8	42.0				
12[b]	140.3	145.8	135.7	131.8	132.6	132.5	183.4				
13[b]	141.9	147.9	135.2	132.3	132.6	132.4	182.0	44.5	20.1		

[a] For $MeCO_2$ groups: δ 24.4, 22.0; 177.3, 174.8. [b] In $(CD_3)_2SO$.

Table 5 Co-ordination chemical shifts, Δδ*/ppm

Complex	C^1	C^6	C^7	C^8
2a	19.4	16.7	17.3	4.8
2b	20.4	16.8	18.0	4.5
2c	22.1	17.2	18.0	3.8
3a	24.0	1.3	16.7	5.6
3b	20.7	2.6	16.9	5.3
3c	20.5	2.5	17.2	5.1
3f	24.2	23.0	21.3	7.9
4	18.5	10.2	12.1	8.8
5a	18.2	11.8	11.7	8.4
5b	18.4	10.6	10.8	7.5
6a	28.0	5.2	12.32	8.5
10a	32.7	10.1	17.1	13.0
10b	32.8	8.45	17.3	13.1

* $\Delta\delta = \delta(\text{complex}) - \delta(\text{aromatic ligand})$.

bond lengths are sensibly different with that *trans* to the phenyl group being the longer, as expected on *trans*-influence grounds. For **10a** the Au–Cl bond length is closely similar to the longer of the two bonds in **6a**, suggesting that the carbon donor atom of the tridentate ligand in **10a** has a similar *trans* influence to that of the analogous bidentate ligand in **6a**. However, the tridentate co-ordination results in a slightly shorter Au–C bond, while the Au–N bonds are a little longer.

Acetate complexes

The complex $[AuCl_2(dmamp)]$ reacted readily with silver acetate to give a diacetato complex with considerably enhanced aqueous solubility.[5,6] For the present compounds, stable products were obtained from complexes **5a** and **6a**, containing the dmamp analogues (the reaction of **4a** was not attempted). These products, **5b** and **6b**, like $[Au(O_2CMe)_2(dmamp)]$, were rather light sensitive. The oxazoline complexes **1a**–**3a** all decomposed to metallic gold in the presence of silver acetate, even when light was rigorously excluded. Similar decomposition occurred in other reactions of these complexes (see above), and was attributed to loss of the oxazoline group. The most likely reaction is conversion of the oxazoline into a carboxylic acid derivative. In principle, this group could bind to gold, forming a five-membered ring; it appears that this system is not stable, at least when the other ligands are hard (*e.g.* halide, acetate).

Complex **6b** was prepared only on a very small scale, and no spectroscopic data were recorded. For **5b**, the carboxylate infrared vibrations were observed at 1599, 1313 and 1502, 1370 cm^{-1}, which are assigned to acetate ligands *trans* to nitrogen and to carbon, respectively. Distinct NMR signals were also seen for the two acetate groups (Tables 3 and 4). As for $[Au(O_2CMe)_2(dmamp)]$, the pairs of ^{13}C signals were of different intensity; the pair with the higher chemical shifts (δ 24.4, 177.3) was broader and less intense than the second set (δ 22.0, 174.8). A detailed study of the dmamp system[6] showed

Table 6 Carbon-13 NMR data for sulfonamide and amide derivatives in $(CD_3)_2SO$

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
$[HgCl(C_6H_4SO_2NMe_2\text{-}2)]$	144.3	155.9	136.5	142.5	132.9	133.0	44.8		
11 $[AuCl_2(C_6H_4SO_2NMe_2\text{-}2)]$	142.0	146.1	137.2	138.5	130.4	134.6	51.8		
$[HgCl\{C_6H_4C(O)NH_2\text{-}2\}]$	155.1	141.5	141.4	131.5	135.4	131.5	174.6		
12 $[AuCl_2\{C_6H_4C(O)NH_2\text{-}2\}]$	145.7	140.3	135.7	131.8	132.6	132.5	183.4		
$[HgCl\{C_6H_4C(O)NHEt\text{-}2\}]$	155.6	141.8	140.9	131.4	131.5	135.1	172.3	38.4	18.5
13 $[AuCl_2\{C_6H_4C(O)NHEt\text{-}2\}]$	147.7	141.9	141.7	131.2	132.4	134.6	181.8	44.3	19.9

Table 7 Selected bond lengths (Å) and angles (°) for complexes **1a** and **6a**

	1a	**6a**
Au–Cl(1)	2.350(3)	2.367(8)
Au–Cl(2)	2.277(3)	2.269(8)
Au–C(1)	2.040(8)	2.08(2)
Au–N	2.051(8)	2.05(3)
Cl(1)–Au–Cl(2)	90.2(1)	87.8(3)
Cl(1)–Au–N	96.1(2)	95.0(7)
Cl(2)–Au–C(1)	92.0(3)	97.6(8)
N–Au–C(1)	81.7(3)	80(1)

Table 8 Selected bond lengths (Å) and angles (°) for $[AuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2[Hg_2Cl_6]$ **10a**

Cation		Anion	
Au(1)–N(1)	2.11(2)	Hg(1)–Cl(2)	2.367(6)
Au(1)–N(2)	2.12(1)	Hg(1)–Cl(3)	2.366(7)
Au(1)–Cl(1)	2.369(6)	Hg(1)–Cl(4)	2.651(6)
Au(1)–C(1)	1.96(2)	Hg(1)–Cl(4*)	2.643(5)
Cl(1)–Au(1)–N(1)	97.8(4)	Hg(1)–Cl(4)–Hg(1*)	88.4(2)
Cl(1)–Au(1)–N(2)	98.3(4)	Cl(2)–Hg(1)–Cl(3)	137.2(2)
N(1)–Au(1)–C(1)	82.0(7)	Cl(2)–Hg(1)–Cl(4*)	103.7(2)
N(2)–Au(1)–C(1)	82.0(7)	Cl(2)–Hg(1)–Cl(4)	107.6(2)
		Cl(3)–Hg(1)–Cl(4*)	106.9(2)
		Cl(3)–Hg(1)–Cl(4)	100.6(2)
		Cl(4)–Hg(1)–Cl(4*)	91.6(2)

* The asterisk denotes the symmetry-related position $1 - x$, $2 - y$, $1 - z$.

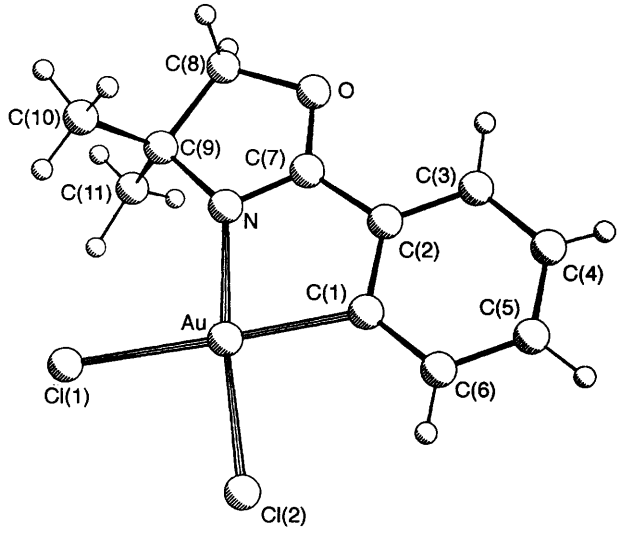


Fig. 1 Molecular structure of complex **1a**

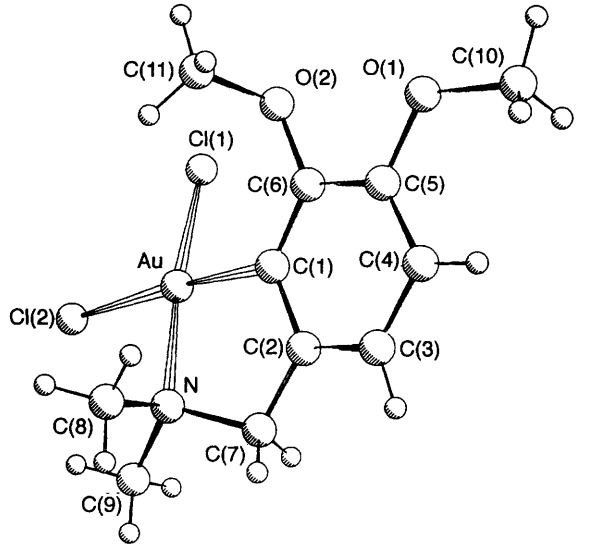


Fig. 2 Molecular structure of complex **6a**

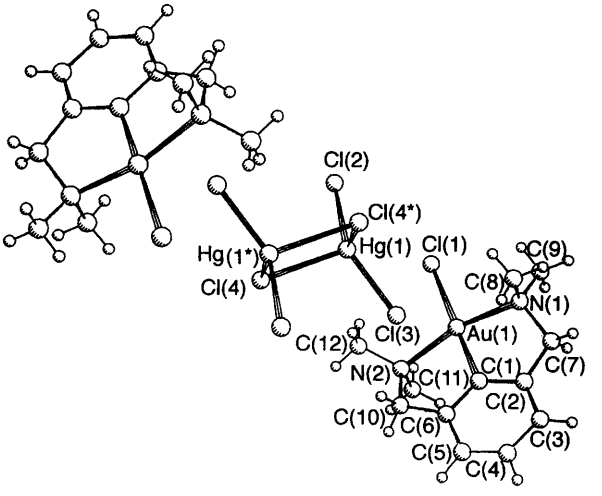


Fig. 3 Molecular structure of complex **10a**

that this behaviour is due to hydrolysis by adventitious traces of water in the $CDCl_3$ solvent used. The acetate group *trans* to carbon undergoes exchange with water at a rate comparable to the NMR time-scale.

In a reaction parallel to that of its dmamp analogue,[19] complex **6b** reacted readily with 2 molar equivalents of pyridinium perchlorate to give the dicationic complex $[Au\{C_6H_2(CH_2NMe_2\text{-}2)(OMe)_2\text{-}5,6\}(py)_2]ClO_4$ **6c** (py = pyridine) for which spectroscopic data were not obtained.

Dithiocarbamate complexes

Reaction of the oxazoline complexes **1a**, **2a**, **3a** or the aminomethylnaphthyl complex **8a** with one molar equivalent of sodium diethyldithiocarbamate, followed by addition of sodium hexafluorophosphate or tetraphenylborate, gave solids **1f**, **2e**, **2f**, **3e** and **8b**. These materials behaved as 1 : 1 electrolytes in acetone (Λ_M = 120, 124 and 122 S mol^{-1} for the PF_6^- salts **1f**, **2f** and **3g**). The infrared spectra (Table 2) confirm that the oxazoline groups remain co-ordinated to gold. The C–N stretching frequencies of the S_2CNEt_2 ligands are similar to those of other gold(III) complexes containing chelated

dithiocarbamate ligands (Table 9) Monodentate dithiocarbamates, such as the gold(I) complexes $[Au(S_2CNR_2)_2]^-$, give lower frequencies (1488–1506 cm^{-1}, R = Me, Et, Pr^n or Bu^n).[20] Nevertheless, as in the corresponding dmamp complexes,[5] it is expected that the two Au–S bonds would be different in length, that *trans* to the carbon atom being longer; the two C–S bonds are presumably also inequivalent.

The lack of planes of symmetry in these molecules, and in the S_2CNEt_2 units in particular, is reflected in the ^{13}C NMR spectra, where the ethyl groups are not equivalent (Table 10). These non-equivalences are barely resolved in the ^1H spectra. The presence of an S-donor ligand *trans* to C^1 increases the co-ordination chemical shift values (owing to the change in solvent the closest values for comparison are those for **11**–**13**, Table 6). The chemical shifts for the carbon atoms of the oxazoline rings, C^7 and C^8, also confirm that the oxazoline group remains co-ordinated, as does the NMe_2 group in **8b**.

Complex **2a** reacts with 2 molar equivalents of NaS_2CNEt_2 to give **2g**. The spectroscopic properties of this complex are markedly different from those of the monodithiocarbamate complexes. In the infrared spectrum (Table 2) the typical C–N band of the oxazoline group occurs at a frequency (1643 cm^{-1}) comparable to that of the free aromatic and of the mercury(II) derivative (1649, 1645 cm^{-1} respectively) and about 30 cm^{-1} higher than for the other gold(III) complexes reported here. This strongly suggests that the oxazoline group is no longer co-ordinated to gold. The S_2CNEt_2 ligands show a single broad C–N stretching band at about 1531 cm^{-1}, about 30 cm^{-1} lower than the corresponding band for **2e**.

The ^{13}C NMR spectrum also indicates that the oxazoline group is not co-ordinated: the chemical shifts of its carbon atoms occur at markedly lower chemical shifts than for any of the other oxazoline derivatives (Table 10). On the other hand the chemical shift for C^1 has decreased substantially compared to those of **2e** and **2f**, which also suggests a change in the mode of co-ordination of the aryl ligand. Only a single set of signals is found for the two S_2CNEt_2 ligands; there is no sign of non-equivalence for the ethyl groups, and the CS_2 carbon atom appears as a single sharp signal. While it is possible that this could indicate five-co-ordination for the gold, with two bidentate S_2CNEt_2 ligands, it is more likely that one dithiocarbamate is monodentate. In the case of the corresponding dmamp complex it was shown crystallographically[5] that, in the solid state, one S_2CNEt_2 was monodentate. The solution behaviour was explained by fast alternation of the two S_2CNEt_2 ligands between mono- and bi-dentate binding.

Table 9 The ν(C–N) bands (cm^{-1}) for dithiocarbamate complexes

Compound	ν(C–N)	Compound	ν(C–N)
1e	1552	$[AuMe_2(S_2CNMe_2)]$[a]	1553
2e	1558[b]	$[AuMe_2(S_2CNEt_2)]$[a]	1538
3e	1535	$[Au(S_2CNMe_2)(dmamp)]BPh_4$[c]	1568

[a] Ref. 20. [b] The PF_6^- and BPh_4^- salts gave the same value. [c] Ref. 5.

Discussion

The stability of the five-membered AuC_3N chelate ring demonstrated by Vicente and co-workers for the dmamp complexes[7,8,11–14] extends to the other complexes shown here, in the ring-substituted analogues of dmamp and its tridentate analogue, and the oxazoline ligands. Two six-membered-ring systems have also been obtained, in the aminomethylnaphthyl derivatives **8** and **9**. The susceptibility to nucleophilic attack of the oxazoline group, which makes it an easily removed protecting group in organic chemistry, is still evident and may even be enhanced by co-ordination. Substitution reactions which, in other complexes, are rapid and quantitative resulted in the production of gold metal; the organic products of these reactions were not identified.

The chloro-complexes were obtained by transmetallation from the corresponding arylmercury compounds. The original preparation of $[AuCl_2(dmamp)]$ employed $[AuCl_3(tht)]$ (tht = tetrahydrothiophene) as the gold-containing starting material and acetone as the solvent.[7] We have found $[NMe_4][AuCl_4]$ to be better.[6b] The reaction is also markedly solvent dependent, being more efficient in polar solvents such as acetonitrile and dimethyl sulfoxide. Although the mechanism of the transmetallation reaction seems not to have been studied, it is likely in this case to proceed *via* formation of a bimetallic intermediate, by co-ordination of the N-donor group to gold (Scheme 2). The role of the solvent may be to inhibit association of the N-donor group with the mercury atom. This would also be consistent with the failure to obtain successful metallation with $[AuCl_4]^-$ and lithium aryls, when the aryl carries a substituent which is a potential ligand;[7] presumably the binding of the ligand group to gold is inhibited by its binding to the lithium cation.

The most interesting reactions of the chloro-complexes are those with dithiocarbamates. Even when the stoichiometry is strictly controlled to be 1:1, both chloride ligands are replaced; the single S_2CNEt_2 ligand chelates to gold(III), giving square-planar CNS_2-co-ordinated cations (Scheme 3). The soft S_2CNEt_2 nucleophile binds to the gold directly, and does not attack the oxazoline group, which remains co-ordinated. Addition of a second S_2CNEt_2 ligand gives products which also retain the oxazoline group but it is no longer co-ordinated. Although the two S_2CNEt_2 ligands appear equivalent in the NMR spectra, it is very likely that one is bi- and the other mono-dentate, with a rapid exchange between them. This non-

Table 10 Carbon-13 NMR data for diethyldithiocarbamate complexes in $(CD_3)_2SO$

												Dithiocarbamate		
Complex	R	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	CS_2	CH_2	CH_3
1e		152.3	132.7	132.8	132.0	133.0	139.2	183.9	87.1	70.7	30.8		197.1	51.2	16.1
														50.7	15.9
2e	5-OMe	154.1	124.0	117.5	118.5	168.1	135.1	183.7	87.1	70.7	31.1	60.3	183.7	51.3	16.4
														50.9	16.1
2f	5-OMe	154.1	124.1	118.5	117.6	166.0	135.1	183.8	87.2	70.8	31.2	60.4	197.3	51.4	16.4
														50.9	16.2
2g	5-OMe	147.2	123.1	112.4	116.7	161.4	130.7	163.8	79.2	67.7	28.4	55.6	200.9	47.1	12.5
3e	5-NMe_2	153.9	115.3	113.8	114.1	147.3	134.0	183.9	86.7	70.1	31.2	58.4	197.6	51.2	16.4
														50.8	16.1
8b[a]		143.9	135.9	133.9	132.5	129.9	130.9	133.9	134.6	138.2	130.7	68.8	196.1	52.1	16.6
														51.1	16.3
b		152.8	152.2	128.7	132.0	131.7	132.9	77.1	56.6				195.5	48.4	12.7
														47.1	12.4

[a] For NMe_2, δ 57.4. [b] $[Au(S_2CNEt_2)(dmamp)]BPh_4$.[5]

equivalence has been demonstrated crystallographically for the dmamp complex,[5] and is similar to the behaviour of the bis-dmamp complex $[AuCl(dmamp)_2]$.[21] In the latter complex the dmamp ligands switch rapidly between mono- and bidentate co-ordination at room temperature (Scheme 4) but the exchange slows sufficiently at 230 K to allow observation of separate NMR signals for the two ligands. This exchange is postulated to occur by dissociation and rebinding of the chloride ligand; the cation $[Au(dmamp)_2]^+$ has been isolated as the perchlorate. The S_2CNEt_2 case might be analogous, involving an intermediate (**14**, Scheme 3) with two monodentate S_2CNEt_2 ligands and a chelating N, C ligand. However, the ^{13}C NMR spectrum of $[Au(S_2CNEt_2)(dmamp)]$ at 230 K shows broadening of the S_2CNEt_2 signals but none for those of the CH_2NMe_2 group;[5] equally there is no change in the position of these latter signals. It is therefore probable that the N,C ligands remain monodentate and that the S_2CNEt_2 exchange occurs through a five-co-ordinate intermediate containing two bidentate S_2CNEt_2 ligands (**15**).

Experimental

Elemental analyses were carried out by the UMIST Chemistry Department Microanalytical Service and the positive-ion fast atom bombardment mass spectra were recorded by the UMIST Centre for Mass Spectrometry; *m/z* values are quoted for ^{35}Cl. Infrared spectra (4000–300 cm^{-1}) were recorded on a Nicolet 5PC Fourier-transform spectrometer in Nujol mulls between KBr plates, ^1H and ^{13}C NMR spectra on a Bruker AC-200 spectrometer at respectively 200 and 50.3 MHz in $CDCl_3$ or $(CD_3)_2SO$ at 25 °C using the solvent signal as internal standard. The ^1H and ^{13}C spectra of complex **1a** were fully assigned by use of homo- and hetero-nuclear correlated two-dimensional spectra. It was assumed that the chemical shifts are in the same order for the substituted gold complexes.

Syntheses

The chloro-complexes **1a–7** were prepared as follows: the appropriate organomercury(II) precursor[10] (5 mmol), tetramethylammonium tetrachloroaurate(III) (5 mmol) and tetramethylammonium chloride were stirred in anhydrous acetone or acetonitrile (40 cm^3) at room temperature for 2 d, during which a white precipitate was formed, $[NMe_4][Hg_2Cl_6]$. The reaction mixture was filtered, and the solid carefully washed with anhydrous acetone or acetonitrile (2 × 15 cm^3). The solvent was removed from the combined extracts under reduced pressure, and the remaining solid extracted into CH_2Cl_2 (3 × 40 cm^3). The solution was left to evaporate slowly, depositing 34–43 mmol of yellow *crystals*.

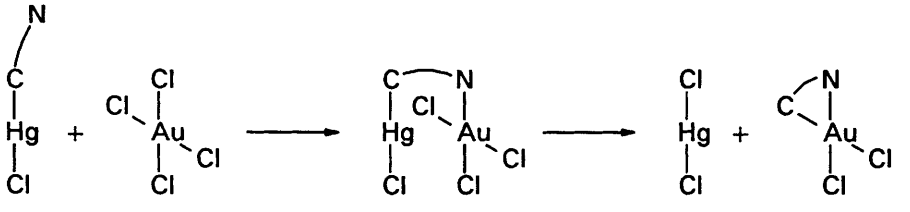
Complexes **8a–10a** were prepared in a very similar manner. Sodium tetrachloroaurate(III) was used instead of the tetramethylammonium salt and no NMe_4Cl was added to the reaction mixture. The complexes **8a** and **9** did not crystallise, but white cubic *crystals* were obtained from the slow evaporation of an acetone solution of **10a**.

Complex **10b** was obtained from [2,6-bis-(*N*,*N*-dimethylaminomethyl)phenyl]chloromercury(II) dihydrochloride (5 mmol) and $Na[AuCl_4]$ (5 mmol), which were dissolved and stirred in water (40 cm^3) for 1 h. The bright yellow *precipitate* obtained was filtered off, washed with water (2 × 15 cm^3), dried in *vacuo* and crystallised from acetone (3.9 mmol).

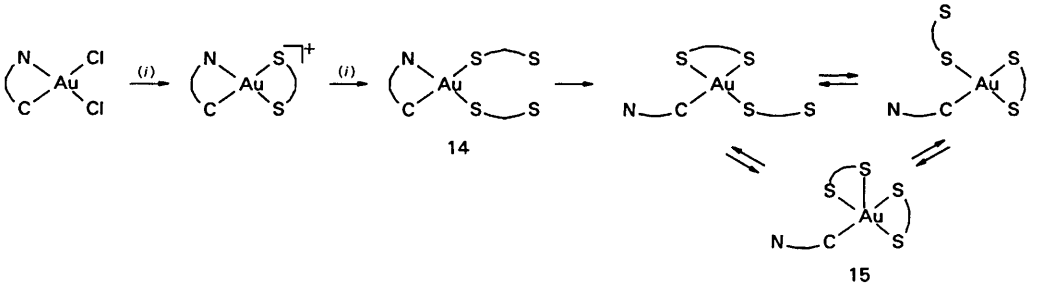
Complexes **5b** and **6b** were prepared by stirring for 2 h a suspension of the appropriate *cis*-dichloroorganogold(III) complex **5a** or **6a** (0.5 mmol) and silver acetate (1 mmol) in dry acetone (30 cm^3). The solution was filtered, the solvent evaporated under reduced pressure and the residue extracted into dichloromethane (3 × 20 cm^3). Evaporation of the solvent left 0.37 mmol of a white *solid*.

Complex **6c** was synthesised by stirring a suspension of **6b** (0.3 mmol) and pyridinium perchlorate (0.7 mmol) in dichloromethane (20 cm^3) for 3 h. The excess of pyridinium perchlorate was filtered off and the solution left slowly to evaporate, depositing 0.13 mmol of white *crystals*. **CAUTION**: perchlorates are potentially explosive, and should be handled with care and only in small quantities.

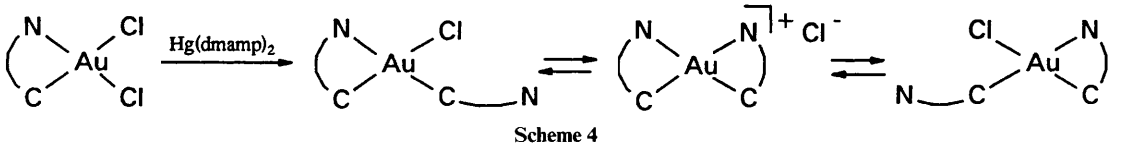
Complexes **1b–1d**, **2b–2d** and **3b–3d** were prepared as follows: A suspension of the appropriate *cis*-dichloroorganogold(III) complex **1a–3a** (0.4 mmol) and either lithium bromide (0.8 mmol), potassium iodide (0.8 mmol) or potassium thiocyanate (0.8 mmol) in acetone (30 cm^3) was stirred for 3 h. The solvent was removed under reduced pressure, and the remaining solid



Scheme 2



Scheme 3 (*i*) NaS_2CEt_2



Scheme 4

Table 11 Experimental data for the crystallographic analyses

	1a	**6a**	**10a**
Formula	$C_{11}H_{12}AuCl_2NO$	$C_{11}H_{16}AuCl_2NO_2$	$C_{24}H_{38}Au_2Cl_8Hg_2N_4$
M	442.09	462.13	1461.32
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	8.371(4)	9.461(2)	9.848(3)
b/Å	14.624(3)	8.895(3)	18.778(7)
c/Å	10.630(3)	16.604(4)	9.894(3)
β/°	96.28(3)	92.00(3)	92.95(3)
U/Å^3	1294(1)	1397(1)	1827(2)
Z	4	4	2
D_c/Mg m^{-3}	2.270	2.198	2.2656
No. reflections for lattice parameters	25	19	25
θ Range/°	26.33–35.92	14.41–20.33	16.01–23.75
F(000)	824	872	1328
Crystal size/mm	0.20 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.25 × 0.25 × 0.25
μ/mm^{-1}	117.33	108.77	169.70
Absorption correction (minimum, maximum)	0.91, 1.08	0.97, 1.03	0.94, 1.08
ω-Scan speed/° min^{-1}	8.0	8.0	2.0
ω-Scan width/°	1.13 + 0.30 tan θ	1.18 + 0.30 tan θ	1.21 + 0.30 tan θ
θ Range/°	0–25.5	0–20.25	0–25
h,k,l Ranges	0–9, 0–16, −12 to 12	0–6, 0–8, −15 to 15	0–10, 0–22, −11 to 11
No. measured reflections	2553	1449	3474
No. reflections used in refinement [$I > 3\sigma(I)$]	1425	751	1872
R_{int}	0.064	0.140	0.064
Goodness of fit	1.036	3.302	1.895
Maximum shift/error	0.08	1.07	1.85
Minimum, maximum height in final ΔF map/e Å^{-3}	−0.59, 0.64	−1.17, 1.07	−1.40, 1.85
R	0.028	0.046	0.045
R'	0.030	0.057	0.054
c in $w = [\sigma^2(F_o) + cF_o^2]^{-1}$	0.030	0.020	0.030

extracted into dichloromethane (3 × 15 cm^3). The solvent was evaporated from the combined extracts to give the *substituted products* as dark orange (**1b**, **2b**, **3b**), dark red (**1c**, **2c**, **3c**) and pale yellow solids (**1d**, **2d**, **3d**).

Complexes **1e**, **2e**, **2f** and **3e** were prepared from the appropriate *cis*-dichloroorganogold(III) (0.4 mmol) dissolved in methanol (40 cm^3). To this solution was added sodium diethyldithiocarbamate (0.4 mmol). The mixture was stirred for 2 h, and a solution of ammonium hexafluorophosphate (0.5 mmol) or sodium tetraphenylborate (0.5 mmol) in methanol (15 cm^3) was added. The solution was stirred for 30 min, filtered and the solvent evaporated under reduced pressure. The residue was extracted into acetone (30 cm^3) and the solution was left to evaporate, depositing approximately 0.25 mmol of white *crystals*.

Complex **2g** was prepared by stirring **2a** (0.5 mmol) and NaS_2CNEt_2 (1 mmol) for 1 h in acetone–methanol (1:2, 50 cm^3). The solvent was removed under reduced pressure and the remaining solid extracted into dichloromethane (30 cm^3). The solution was concentrated to 10 cm^3 and *complex* **2g** was crystallised by addition of diethyl ether (5 cm^3).

Complexes **1e** and **3f** were prepared by adding PPh_3 (0.5 mmol) in dichloromethane (10 cm^3) to the dichloro-complex **1a** or **3a** (0.5 mmol) in the same solvent (40 cm^3) and stirring the mixture for 1 h. The solution was then concentrated to about 15 cm^3 and diethyl ether added (*ca.* 10 cm^3); the *products* slowly crystallised.

Crystallography

Suitable crystals of complexes **1a**, **6a** and **10a** were obtained by slow evaporation of the solvent from a dichloromethane (**1a** and **6a**) or acetone solution (**10a**). X-Ray diffraction measurements were performed at room temperature on a RIGAKU AFC6S diffractometer using graphite-monochromatised Mo-Kα radiation. The structures were solved by direct methods using SHELXS.[22] The structures were subjected to full-matrix least-squares refinement based on F. Non-hydrogen atoms were treated anisotropically and hydrogen atoms were constrained to chemically reasonable positions. No reflections were recorded above 40° for **6a** because of its poor crystallinity, which also led to a high R_{int} value and necessitated isotropic refinement of the nitrogen and several carbon atoms. Crystallographic data are given in Table 11.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/123.

Acknowledgements

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