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Organogold(III) Metallacyclic Chemistry. Part 3[1]. Self-assembly of the nonametallic gold(III)-silver(I)-sulfido aggregates $[\{LAu(\mu\text{-}S)_2AuL\}_3Ag_3X_2]^+$ (L = cycloaurated N,N-dimethylbenzylamine ligand; X = Cl, Br), by thiourea desulfurisation

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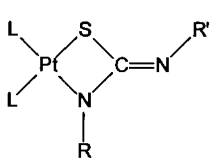
Abstract

Reaction of the gold(III) dihalide complexes $[\{C_6H_3(CH_2NMe_2)\text{-2-R-5}\}AuX_2]$ (R = OMe, H; X = Cl, Br) with *N*,*N′*-dimethylthiourea and silver(I) oxide in refluxing dichloromethane gave the novel gold(III) aggregate cations $[\{[\{C_6H_3(CH_2NMe_2)\text{-2-R-5}\}Au(\mu\text{-}S)]_2\}_3Ag_3X_2]^+$, formed from the desulfurisation of the thiourea. The cations consist of three gold sulfide dimers doubly-bridged by three silver(I) cations, which in turn are triply-bridged by two halides. The aggregates have been fully characterised by ^{1}H- and ^{13}C-NMR spectroscopy and electrospray mass spectrometry (ESMS), which showed very strong parent ions that proved remarkably resilient to cone voltage induced fragmentation. Single crystal X-ray structures have been determined for two examples, although the nature of the counter-anion could not be unambiguously determined. The two X-ray studies show that both *cis* and *trans* isomers (with respect to the orientation of the *N*,*N*-dimethylbenzylamine ligands on either side of the Au_2S_2 group) form, although only one isomer was isolated in each case. To compare this chemistry with that of platinum(II), *cis*-$[PtCl_2(PPh_3)_2]$ and *N*,*N′*-dimethylthiourea were reacted in the presence of silver(I) oxide. Only the expected thiourea dianion complex $[Pt\{SC(=NMe)NMe\}(PPh_3)_2]$ formed, as observed in previously reported studies. The formation of the gold(III)-sulfido aggregates clearly demonstrates that gold(III) can have remarkably different chemistry to that of platinum(II). Reaction of $[\{C_6H_3(CH_2NMe_2)\text{-2-OMe-5}\}AuCl_2]$ with *N*,*N′*-diphenylselenourea in the presence of silver(I) oxide failed to give analogous selenium aggregates. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Gold; Silver; Sulfide; Aggregate; Thiourea; Desulfurisation; Electrospray mass spectrometry

1. Introduction

Thioureas and selenoureas, of the general formula $R^1R^2N\text{–}C(S/Se)\text{–}NR^3R^4$, are interesting hybrid ligands, containing both hard (nitrogen) and soft (sulfur or selenium) donor atoms, and are therefore able to coordinate to a wide range of metal centres [1]. Such ligands are well-known to coordinate to metal centres either as neutral ligands [1,2] or as monoanions [1,3]. In marked contrast however, complexes containing thiourea dianion ligands are much rarer; examples of platinum **1**



1a R = Ph; R' = Ph; L = tertiary phosphine

1b R = Et; R' = Et; L = PPh_3

1c R = Me; R' = CN; L = tertiary phosphine

1d R = Me; R' = Me; L = PPh_3

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[1] For parts 1 and 2 see references [10] and [11].

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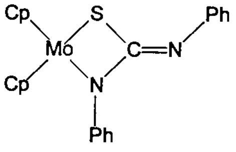
[4–6] and molybdenum **2**



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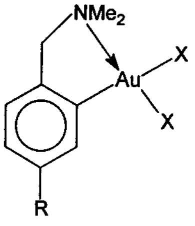
[7] complexes have been described. We are currently investigating the synthesis and chemistry of transition metal complexes containing thiourea dianions, and are exploring the use of the reagent silver(I) oxide for the formation of such complexes [4,5].

Gold(III) is isoelectronic with platinum(II) (d^8), but it is more electronegative and more strongly oxidising, and its metallacyclic chemistry is only poorly explored. We have recently used the gold(III) dichloride complexes



3a R = OMe; X = Cl

3b R = H; X = Cl

3c R = OMe; X = Br

3d R = H; X = Br

[8,9] (containing an ancillary cyclometallated *N*,*N*-dimethylbenzylamine ligand) for the synthesis of new gold(III) metallacyclic complexes [10,11]. In this paper we report our studies on the reactions of the cyclometallated complexes **3a**, **3b** and some related complexes, with disubstituted thioureas and with *N*,*N*′-diphenylselenourea, mediated by silver(I) oxide.

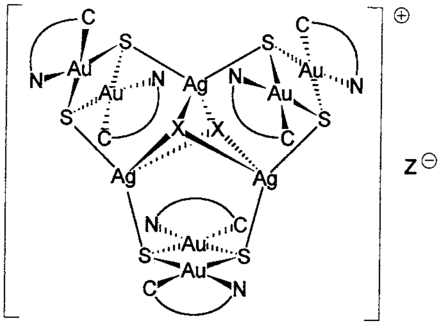
2. Results and discussion

2.1. Synthesis

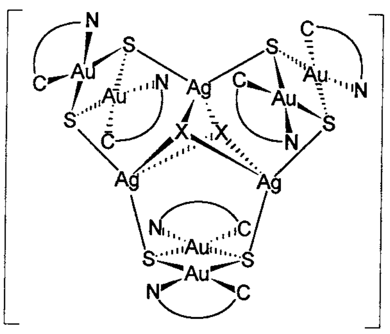
The reactions of the gold(III) dihalide complexes $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}5\}AuX_2]$ (R = OMe, H; X = Cl, Br) **3a–3d** with *N*,*N*′-dimethylthiourea and an excess of silver(I) oxide in refluxing dichloromethane rapidly (ca. 5 min) lead to bright yellow solutions. The mixtures were reacted for a further 4 h from which bright yellow crystals of the aggregates **4a–d**, respectively, could be obtained. The complexes were characterised by ^{1}H- and ^{13}C-NMR, electrospray mass spectrometry (ESMS), elemental analysis, and by single crystal X-ray diffraction studies for **4a** and **4d**. Assignment of the different configurations with regard to the *N*,*N*-dimethylbenzylamine ligands in **4a**/**4c** versus **4b**/**4d** of the isolated complexes is described later. The synthesis of the analogous diiodide-bridged aggregate was not attempted, because of the difficulty in the isolation and manipulation of the starting gold(III) iodide $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}OMe\text{-}5\}AuI_2]$ which was found to be exceedingly light-sensitive.

When *N*,*N*′-diphenylthiourea was reacted with **3a** in the presence of silver(I) oxide, the aggregate **4a** could also be successfully isolated. However, the reaction appeared to have poor reproducibility, with success in only one of four reaction attempts.

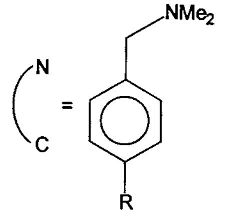
The synthesis of the sulfido-aggregates **4a–4d** clearly demonstrates markedly different behaviour between the formally isoelectronic platinum(II) and gold(III) centres towards thioureas; no analogous aggregate complexes have ever been observed in platinum(II) reactions with thioureas (specifically *N*,*N*′-diphenylthiourea), these always giving metallacycles **1**. However, the silver(I) oxide mediated reaction of *N*,*N*′-dimethylthiourea with a platinum(II) halide had not been previously attempted. To verify the expected product, $[Pt\{SC({=}NMe)NMe\}(PPh_3)_2]$ **1d**, the reaction of *cis*-$[PtCl_2(PPh_3)_2]$, *N*,*N*′-



4a R = OMe; X = Cl
4c R = OMe; X = Br

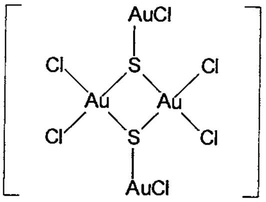


4b R = H; X = Cl
4d R = H; X = Br



dimethylthiourea and silver(I) oxide was undertaken and, as predicted, **1d** was the only product formed. The ^{1}H-NMR of complex **1d** shows both the predicted ^{195}Pt–^{1}H and ^{31}P–^{1}H couplings to the methyl group closest to the metal centre.

Complexes containing μ-sulfido and -selenido bridges between transition-metal centres have attracted considerable interest for their structures [12], nucleophilicity towards alkylation [13], catalytic activities [14] and ability to act as 'metallo-ligands' towards other metal centres, building up unusual sulfido-bridged coordination assemblies [15–17]. A large number of complexes containing the dimeric metal(II)-sulfido/selenido unit $M(\mu\text{-S,Se})_2M$ units (M = Pd or Pt) are known [18–20], and these units have been employed in syntheses of a diverse range of heterobimetallic complexes [21]. A review describing the chemistry of platinum sulfide polynuclear complexes has recently been published [22]. To the best of our knowledge the isoelectronic gold(III) group, $Au(\mu\text{-S})_2Au$, has been described only once previously, in the mixed gold(I)–gold(III) anion $[Au_4Cl_6S_2]^{2-}$ [23], isolated from the reaction between [AuCl(CO)], $Na(SBu^t)$ and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane). The molecular structure of **5** shows the gold(III) sulfide ring coordinating to two –AuCl units. Two X-ray crystal structures of anions containing the related $Au(\mu\text{-Se})_2Au$ unit, in $[(SCH_2CH_2S)Au(\mu\text{-Se})_2Au(SCH_2CH_2S)]^{2-}$ [24] and $[(Se_4)Au(\mu\text{-Se})_2Au(Se_4)]^{2-}$ [25] have been reported, though full details on the former compound have not yet appeared. Examples of gold(III) dimeric complexes containing bridging thiolate ligands, of the type $Au(\mu\text{-SR})_2Au$ are also known [26].



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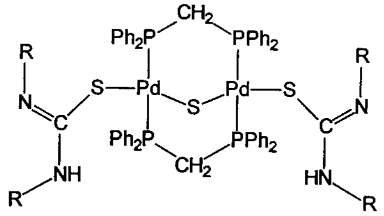


6 R = *o*-tolyl

The formation of the sulfide aggregates from dimethylthiourea presumably results in the formation of dimethyl carbodiimide as a by product, which may be hydrolysed under the reaction conditions to give *N*,*N*′-dimethylurea, though no attempts were made to identify any by-product(s) formed. Desulfurisation reactions of thioureas by metal aggregates are well-documented in the literature [27–29], though we are aware of only one related desulfurisation reaction of a thiourea by a mononuclear complex under mild reaction conditions. Okeya and co-workers recently reported the desulfurisation of a thiourea ligand by palladium(II), forming the sulfide-bridged dimeric complex **6** [30] which highlighted the difference between palladium and platinum systems. Sulfide-bridged platinum and palladium dinuclear complexes have also been prepared by C–S bond fission reactions involving propylene sulfide [31] or thiols [32], respectively. Carbon–sulfur and carbon–selenium bond cleavage reactions are of interest for the formation of metal–sulfide and –selenide solid-state materials having interesting optical and electronic properties [33].

2.2. *X-ray structure analysis of* **4a**

Crystals of compound **4a** suitable for an X-ray structure determination were obtained by layering benzene onto a chloroform solution of **4a** at 4°C. The compound crystallised in the rare cubic space group Pn-3n. The molecular structure of the core of the aggregate is shown in Fig. 1(a) together with the atom numbering scheme. The cation lies on a two-fold axis so there are effectively only two distinct gold 'monomer' units, those formed by Au(1)/Au(2) and Au(3)/Au(3′), and these will be subsequently referred to as monomers 1 and 2, respectively. Monomer 1 is depicted in Fig. 1(b), and selected bond lengths and angles are presented in Table 1.

The aggregate consists of an assembly of three $Au(\mu\text{-S})_2Au$ units (with each gold ligated by a cyclometallated *N*,*N*-dimethylbenzylamine ligand), with the two sulfur atoms coordinated to two of three silver(I) ions. The three silver ions are in turn bound by two μ_3-chloride ligands, above and below the plane defined by the three silvers. The gold monomer units are pivoted at right angles to the silver core, giving butterfly angles between least-squares planes drawn through Au–S–Au–S and Ag–S–S–Ag of 89.8(1) and 90.0(1)° for monomers 1 and 2, respectively. The silver atoms themselves are coordinated in a very distorted tetrahedral configuration, with an average S–Ag–S angle of 131.3(4)°, Cl–Ag–S angle of 107.4(5)° and Cl–Ag–Cl averaging 89.5(4)°.

In contrast to the isoelectronic four-membered Pt–S–Pt-S ring systems with sulfido bridges, which have a strong propensity to adopt hinged structures [12], the monomer units in **4a** are essentially flat, with no atom deviating from the least-squares drawn through N(1), C(11), Au(1), S(1), S(2), Au(2), C(21) and N(2) by more than 0.080(9) Å above, and 0.08(1) Å below the plane

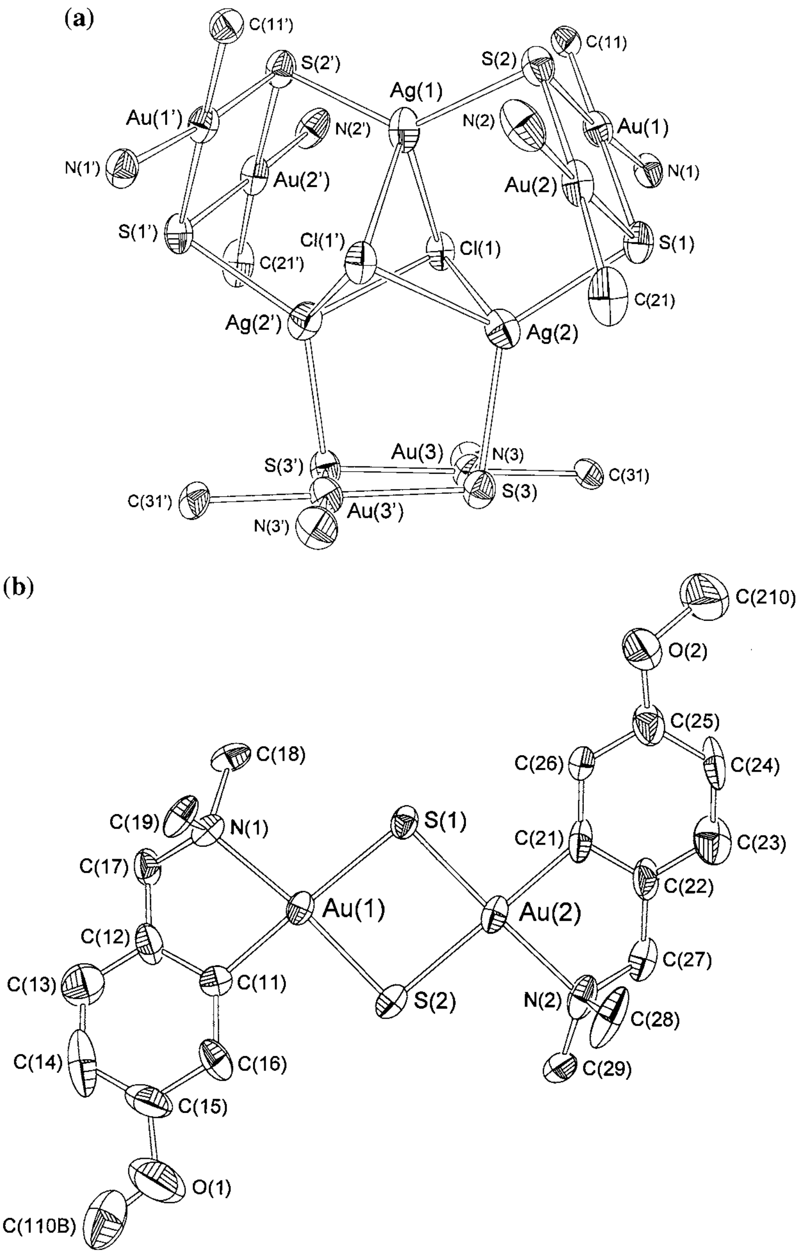


Fig. 1. (a) The molecular structure of the core of the cationic aggregate **4a**, showing the atom numbering scheme (the ′ denotes symmetry related atoms). (b) Monomer 1 from **4a**, illustrating the *trans* configuration of the opposing *N*,*N*-dimethylbenzylamine ligands. All thermal ellipsoids are shown at the 30% probability level.

for C(21) and N(2), respectively. The analogous plane drawn through monomer 2 similarly shows maximum deviations of 0.10(2) Å for N(3) and 0.095(7) for S(3). This is consistent with the only related gold(III) sulfide complex **5**, which was found to be absolutely planar [23]. Many of the platinum(II) bridging-sulfide complexes, where the sulfur is only two-coordinate, have been found to be bent, and a theoretical study for these systems has suggested that the bending occurs in order to decrease through-ring antibonding interactions between in-plane sulfur p-orbitals [12]. This is consistent with observation of sulfide-bridged systems being planar when the sulfurs are co-ordinated to a third moiety which presumably involves the sulfur p-orbitals, and explains the planarity of our gold-sulfide aggregate complexes.

The *N*,*N*-dimethylbenzylamine ligands within the monomer units are coordinated in a *trans* configuration with respect to each other, as seen in Fig. 1(b). The Au–S bond lengths [averaging 2.30(1) Å] *trans* to the *N*,*N*-dimethylamino group are, as expected on *trans*-influence grounds [34], significantly shorter than those *trans* to the aryl carbons [2.39(1) Å]. The S–Au–S angle in **4a** has an average value of 85.4(3)°, compared to 82.91(9)° for **5** [23]. Likewise the average Au–S–Au angles of **4a** [94.6(3)°] resemble the Au–S–Au angle of **5** [97.09(9)°]. The very different *trans*-influence groups of **4a** (N and

Table 1
Selected bond lengths (Å) and angles (°) for **4a** with estimated standard deviations in parentheses

Bond	Length	Bonds	Angle
Core			
Ag(1)–S(2)	2.512(6)	S(2)–Ag(1)–S(2′)	132.9(3)
Ag(2)–S(1)	2.512(6)	S(1)–Ag(2)–S(3)	129.6(2)
Ag(2)–S(3)	2.520(7)	S(2)–Ag(1)–Cl(1)	113.1(2)
Ag(1)–Cl(1)	2.833(6)	S(2)–Ag(1)–Cl(1′)	100.2(2)
Ag(2)–Cl(1)	2.854(6)	S(1)–Ag(2)–Cl(1)	98.1(2)
Ag(2)–Cl(1′)	2.779(6)	S(1)–Ag(2)–Cl(1′)	113.8(2)
Ag(1)···Ag(2)	3.523(4)	S(3)–Ag(2)–Cl(1)	117.9(2)
Ag(2)···Ag(2′)	3.356(4)	S(3)–Ag(2)–Cl(1′)	101.1(2)
Cl(1)···Cl(1′)	3.976(6)	Ag(1)–Cl(1)–Ag(2)	76.5(2)
		Ag(1)–Cl(1)–Ag(2′)	77.8(2)
		Ag(2)–Cl(1)–Ag(2′)	73.1(2)
		Cl(1)–Ag(1)–Cl(1′)	89.2(3)
		Cl(1)–Ag(2)–Cl(1′)	89.8(2)
Gold sulfide monomers			
Au(1)–S(1)	2.389(6)	S(1)–Au(1)–S(2)	85.3(2)
Au(1)–S(2)	2.306(6)	S(1)–Au(2)–S(2)	85.4(2)
Au(2)–S(1)	2.302(6)	S(3)–Au(3)–S(3′)	85.5(2)
Au(2)–S(2)	2.388(7)	N(1)–Au(1)–C(11)	80.8(6)
Au(3)–S(3)	2.293(6)	N(2)–Au(2)–C(21)	83.1(7)
Au(3)–S(3′)	2.382(6)	N(3)–Au(3)–C(31)	80.9(6)
Au(1)–N(1)	2.15(2)	Au(1)–S(1)–Au(2)	94.7(2)
Au(2)–N(2)	2.14(2)	Au(1)–S(2)–Au(2)	94.6(2)
Au(3)–N(3)	2.13(2)	Au(3)–S(3)–Au(3′)	94.4(2)
Au(1)–C(11)	1.973(11)		
Au(2)–C(21)	2.030(11)		
Au(3)–C(31)	2.034(8)		
Ag(1)···Ag(2)	3.451(6)		
Ag(3)···Ag(3′)	3.432(6)		
S(1)···S(2)	3.181(6)		
S(3)···S(3′)	3.174(6)		

C) and **5** (Cl), render bond-length comparisons unjustified.

While the identity of the aggregate cation in **4a** is unambiguous, with further confirmation by electrospray mass spectrometry (vide infra), the identity of the counter-anion (Z^-) is not wholly certain. Residual electron density was located as a large peak and a smaller peak about a three-fold site. Although the larger peak could be modelled reasonably well as a chloride, a better model was to assign this peak as an Ag^+ with partial occupancy and the smaller peak as a partial Cl^-. This then generates a trichloroargentate(I) $[AgCl_3]^{2-}$ ion which, although rare, has been reported previously [35,36], and the Ag–Cl distance of 2.54(2) Å is not unreasonable for this anion. However since there are 16 of these species in the unit cell versus 24 cations, either each anion site is only two-thirds occupied or there are equal numbers of $[AgCl_3]^{2-}$ and $[AgCl_2]^-$, so that total charge in the unit cell is 24 −. Both options are consistent with the elemental analysis results, and fit the data better than a lone Cl^- anion, which would give an insufficient chlorine percentage. However, the quality of the data did not allow the nature of the anion to be unambiguously defined, so the structural determination of the bromide analogue **4d** was also undertaken.

2.3. *X-ray structure analysis of* ***4d***

Crystals suitable for the X-ray study of the bromide-bridged complex **4d** were grown from the slow diffusion of diethyl ether into a dichloromethane solution at −20°C. The structure revealed two independent cations in the unit cell (cations 1 and 2). The core of cation 1 is shown in Fig. 2(a) with one of its constituent monomer units shown in Fig. 2(b), illustrating the atom numbering scheme. Since the independent cations and their constituent monomer units show essentially the same structural parameters, only data from cation 1 (Fig. 2(a)) and the monomer shown in Fig. 2(b) will be discussed; selected bond lengths and angles are presented in Table 2.

Unfortunately the structure did not refine particularly well ($R_1 = 0.1090$), and once again the residual electron density could not be sensibly assigned to anions. In this case only relatively small peaks remained which precluded anions derived from Ag^+ or Br^-. The only sensible suggestion appears to be OH^-, although the elemental analysis results would suggest something heavier. For both these structures, **4a** and **4d**, it seems that the structure is determined by the packing of the very large cations. The associated anions are then accommodated within the gaps between the cations in poorly defined regions. The actual anions in any given preparation are those available in solution and could well vary from preparation to preparation. Some attempts were made to produce well-defined crystals with specific counter-anions such as BPh_4^-, but these did not lead to suitable single crystals.

Despite the high *R* factor, the cation core is nonetheless well-defined, and a number of structural features are noteworthy. The core of the cation **4d** is directly analogous to **4a**, as predicted, with two triply-bridging bromides bonding the silver atoms. Similar to those in **4a**, the monomer gold sulfide units are coordinated at right angles with planes drawn through Au(13), S(13), Au(14) and S(14) and Ag(11), S(13), S(14) and Ag(12) forming an angle of 87.8(1)°. The monomer units themselves are essentially planar, exemplified by the least-squares plane drawn through N(13), Au(13), C(131), S(13), S(14), Au(14), C(146) and N(14) which shows maximum deviations of 0.10(1) Å above [for C(141)] or 0.10(1) Å below the plane [for S(13)].

The most structurally startling feature of **4d** is that the benzylamine ligands in the monomer units in this cation are coordinated *cis* with respect to each other, in contrast to those in **4a**. There is no obvious explanation for the difference, so presumably there is little preference for *cis* or *trans* configurations of the benzylamine

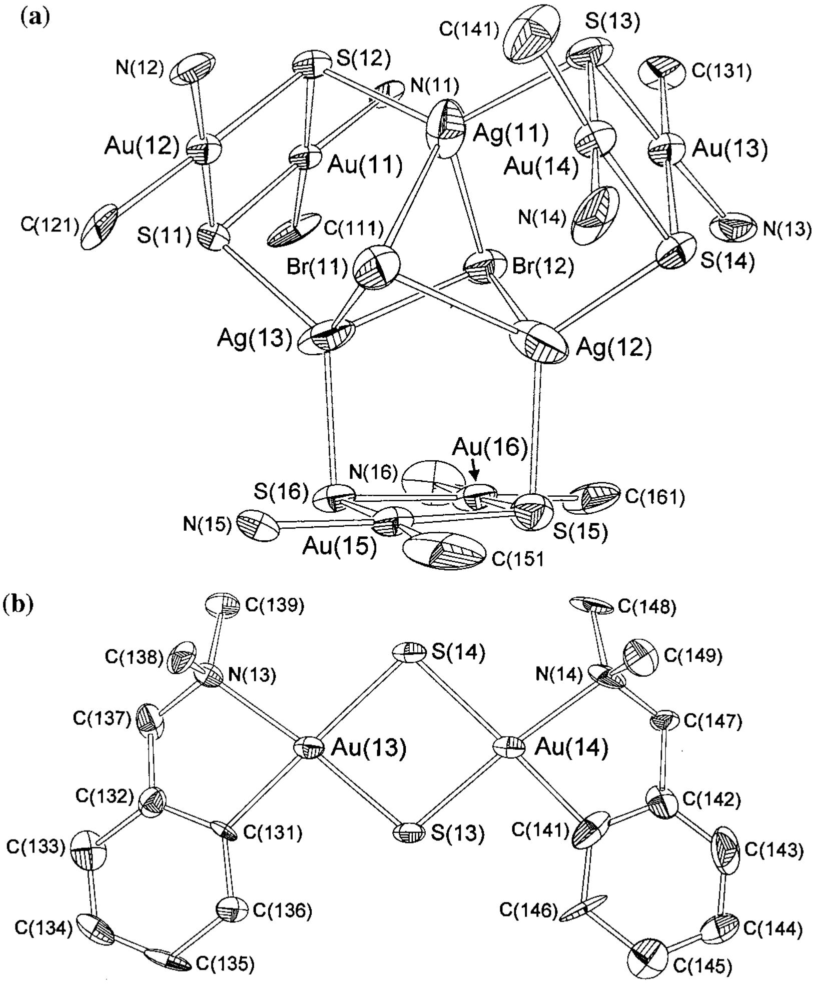


Fig. 2. (a) The molecular structure of the core of the cationic aggregate **4d**, showing the atom numbering scheme. (b) One of the monomer units from **4d**, illustrating the *cis* configuration of the opposing *N*,*N*-dimethylbenzylamine ligands. All thermal ellipsoids are shown at the 30% probability level.

ligands in the monomer formation. We believe that cations containing only *cis* and cations containing only *trans* monomer units form in solution (evidenced by the detection of two species in the crude reaction mixture by NMR), but only one aggregate **4** crystallises out in each case, determined by their relative solubilities and concentrations (yields for **4a**–**4d** were less than 60%). Hence, during the aggregation process the nature (*cis* or *trans*) of the first monomer unit directs the 'selection' of subsequent monomer units for the trimer formation. Since the crystals of aggregate ions when dissolved in $CDCl_3$ are, and remain, absolutely pure, together with the observation that the complexes appear to be very stable in ESMS studies, the aggregation process is most likely not reversible. The complete mechanism for their formation is clearly not obvious.

Like those for **4a**, the Au–S bonds *trans* to N are significantly shorter than those *trans* to C, with average lengths of 2.30(1) and 2.41(1) Å, respectively, although in this case they are *cis* relative to each other. The remainder of the structural parameters (where justified) are comparable to those of **4a**.

2.4. NMR characteristics

As already mentioned, the ^{1}H- and ^{13}C-NMR spectra of the isolated crystalline products reveal them to be completely pure. As expected, the presence of NMe groups and CH_2 protons pointing above and below (with respect to the silver-halide core) the plane of the monomers results in inequivalence of these signals in the ^{1}H- and ^{13}C-NMR spectra. For **4a** the *N*,*N*-dimethylamino protons are split by 0.44 ppm and the carbons by 1.1 ppm. Similarly, the methylene protons are split by 0.73 ppm, and show mutual ^{2}J coupling of 13.22 Hz.

Analysis of the crude reaction products of **4a**–**4d** shows a second complex (ca. 30–50% NMR yield), with spectroscopic properties very similar to those of the isolated complexes. The structure of these complexes has not been confirmed, but in light of the structure of **4d**,

Table 2
Selected bond lengths (Å) and angles (°) for **4d**, specifically for cation 1 and for the monomer unit shown in Fig. 2(b), with estimated standard deviations in parentheses

Bond	Length	Bonds	Angle
Core			
Ag(11)–S(12)	2.494(8)	S(12)–Ag(11)–S(13)	129.5(3)
Ag(11)–S(13)	2.520(10)	S(12)–Ag(11)–Br(11)	105.1(2)
Ag(11)–Br(11)	2.929(5)	S(12)–Ag(11)–Br(12)	103.3(2)
Ag(11)–Br(12)	2.952(5)	Ag(11)–Br(11)–Ag(12)	74.4(1)
Ag(11)···Ag(12)	3.502(5)	Ag(11)–Br(12)–Ag(12)	73.7(1)
Ag(11)···Ag(13)	3.708(5)	Br(11)–Ag(11)–Br(12)	89.4(1)
Ag(12)···Ag(13)	3.457(5)		
Br(11)···Br(12)	4.135(6)		
Gold sulfide monomer			
Au(13)–S(13)	2.304(8)	S(13)–Au(13)–S(14)	84.9(3)
Au(13)–S(14)	2.410(8)	S(13)–Au(14)–S(14)	84.8(3)
Au(14)–S(13)	2.304(8)	N(13)–Au(13)–C(131)	81.0(7)
Au(14)–S(14)	2.411(8)	N(14)–Au(14)–C(141)	81.3(9)
Au(13)–N(13)	2.17(3)	Au(13)–S(13)–Au(14)	97.9(3)
Au(14)–N(14)	2.12(3)	Au(13)–S(14)–Au(14)	92.3(3)
Au(13)–C(131)	2.08(1)		
Au(14)–C(141)	2.05(1)		
Au(13)···Au(14)	3.476(8)		
S(13)···S(14)	3.182(8)		

probably arise from the corresponding aggregate (derived from all *cis* or all *trans* monomer units) not isolated in the recrystallisation process.

The elucidation of the structures **4a** and **4d** allows tentative structural assignment of **4b** and **4c** by NMR. Since the bridging halides are probably too far removed (four bonds to Au–C, the nearest NMR active nucleus) from the benzylamine ligands, the chemical shifts in the ^{1}H- and ^{13}C-NMR are likely to dominated by the *cis*/*trans* configurations of the ligands. The ^{1}H- and ^{13}C spectra for the isolated crystalline aggregates **4a** and **4c** are virtually identical, as are the spectra for **4b** and **4d**, so we propose that the **4b** collected (like **4d**) is also a *cis* isomer, and **4c** (like **4a**) is a *trans* isomer.

2.5. Electrospray mass spectrometry

ESMS is being increasingly used for the characterisation of a diverse range of coordination and organometallic compounds [37,38]. A wide range of metal–sulfur bonded compounds have been analysed by the ESMS technique to date, including metal–chalcogenide–thiolate aggregates [39–42], a polyoxo/thioanion [43] and complexes of thiourea dianions [6]. ESMS is ideally suited for the analysis of charged species, since pre-existing ions present in solution are simply transferred to the gaseous phase for analysis. The soft ionisation process generally results in intact parent ions being observed.

Major ions observed in the ESMS spectra of the aggregates **4a**–**4d** are summarised in Table 3. For complex **4a** at cone voltages of 20–100 V the base peak was due to the aggregate cation $[M_3Ag_3Cl_2]^+$ (M = $[Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}S]_2$) (Fig. 3), and even at a high cone voltage of 150 V this remained a major ion. The presence of one or more elements possessing more than a single isotope provides substantial information in the form of isotope distribution patterns for the ions in question. In the case of the silver–gold aggregates described herein, silver (^{107}Ag 51.8, ^{109}Ag 48.2%), chlorine (^{35}Cl 75.8, ^{37}Cl 24.2%) and bromine (^{79}Br 50.7, ^{81}Br 49.3%) all possess two isotopes in reasonable abundance, giving distinctive isotope patterns for all of the aggregate cations in the complexes **4a**–**4d**. Excellent agreement is observed between the experimental and calculated isotope distribution patterns (exemplified for the $[M_3Ag_3Cl_2]^+$ cation of **4a** shown in the inset of Fig. 3) for all species observed in the spectra of the cations in **4a**–**4d**. These ESMS results indicate that the aggregate cations have very high stability. For complex **4a**, other easily identified minor fragment ions, such as $[M_2Ag_3Cl_2]^+$ and $[M_2Ag]^+$, which become significant only at higher cone voltages, additionally aid in characterisation, and are indicated in Fig. 3.

Table 3
List of ions observed in the positive ion ESMS spectra of complexes **4a**–**4d**

Complex	Cone voltage (V)	Ions *m*/*z*† (identity, relative abundance (%))
4a (R = OMe)	20	2752 ($[M_3Ag_3Cl_2]^+$, 100%), 2357 ($[M_3H]^+$, 7%), 1824 ($[M_2Ag_2Cl]^+$, 10%), 1681 ($[M_2Ag]^+$, 2%), 894 ($[MAg]^+$, 15%), 814 (unidentified, 15%)
	50	2752 ($[M_3Ag_3Cl_2]^+$, 100%), 1968 ($[M_2Ag_3Cl_2]^+$, 6%), 1824 ($[M_2Ag_2Cl]^+$, 8%), 894 ($[MAg]^+$, 17%)
	150	2752 ($[M_3Ag_3Cl_2]^+$, 59%), 1968 ($[M_2Ag_3Cl_2]^+$, 27%), 1824 ($[M_2Ag_2Cl]^+$, 13%), 1681 ($[M_2Ag]^+$, 41%), 1288 (unidentified, 92%), 164 ($[C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5]^+$, 100%)
4b (R = H)	30	2573 ($[M_3Ag_3Cl_2]^+$, 100%), 1846 ($[M_2Ag_3Cl_2]^+$, 3%), 1704 ($[M_2Ag_2Cl]^+$, 59%), 1561 ($[M_2Ag]^+$, 97%)
	100	2573 ($[M_3Ag_3Cl_2]^+$, 100%), 1846 ($[M_2Ag_3Cl_2]^+$, 27%), 1704 ($[M_2Ag_2Cl]^+$, 13%), 1561 ($[M_2Ag]^+$, 17%)
4c (R = OMe)	20	2842 ($[M_3Ag_3Br_2]^+$, 10%), 1681 ($[M_2Ag]^+$, 40%), 661 (unidentified, 100%)
	100	2842 ($[M_3Ag_3Br_2]^+$, 100%), 2056 ($[M_2Ag_3Br_2]^+$, 8%), 1681 ($[M_2Ag]^+$, 39%)
4d (R = H)	50	2662 ($[M_3Ag_3Br_2]^+$, 100%), 1936 ($[M_2Ag_3Br_2]^+$, 6%), 1749 ($[M_2Ag_2Br]^+$, 17%), 1561 ($[M_2Ag]^+$, 13%)
	100	2662 ($[M_3Ag_3Br_2]^+$, 100%), 1936 ($[M_2Ag_3Br_2]^+$, 48%), 1749 ($[M_2Ag_2Br]^+$, 20%), 1561 ($[M_2Ag]^+$, 51%)

All spectra were recorded using methanol as both the solvent and mobile phase. M = $[Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}R\text{-}5\}S]_2$.
† *m*/*z* value refers to peak of greatest intensity in the isotope distribution pattern.

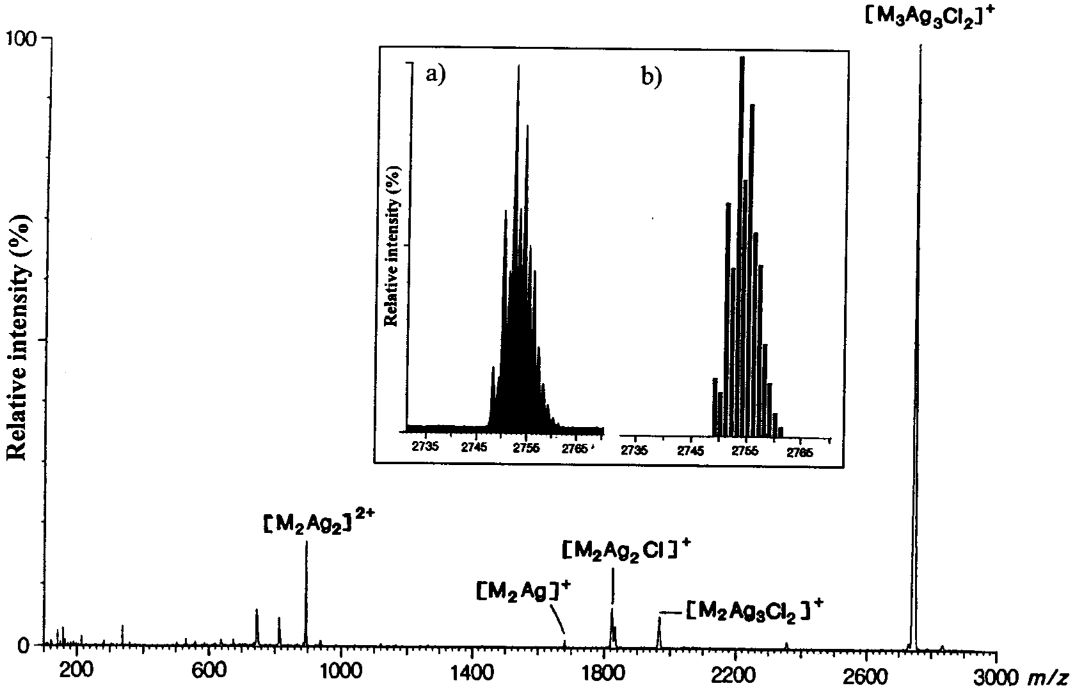


Fig. 3. Positive-ion electrospray mass spectrum of the complex **4a**, recorded in methanol, at a cone voltage of 20 V. The inset shows (a) the observed and (b) the calculated isotope patterns of the parent ion $[M_3Ag_3Cl_2]^+$ ($M = [Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}S]_2$).

Addition of lithium bromide to a solution of **4a** prior to injection into the mass spectrometer indicated ready displacement of the chloride ions by bromide, thereby generating **4c** in situ. No trace of any residual **4a** remained.

2.6. Additional synthetic studies

To develop a more systematic synthesis of the gold–silver aggregates, it was reasoned that the reactions of the gold–dihalide complexes **3a**–**3d** with silver(I) sulfide might be successful. When **3a** and silver(I) sulfide were refluxed in dichloromethane for 28 h, the isolated yellow residue contained at least five compounds by ^{13}C-NMR, none of which corresponded to **4a**. Additionally ESMS showed only trace quantities of the aggregate **4a**, with the spectrum dominated by $[M_2Ag]^+$ (previously observed as a fragment ion of **4a**). However, repeated recrystallisation of the residue by layering benzene on chloroform solutions at 4°, eventually gave bright yellow crystals of **4a**, although in very low yield. A possible explanation for the relative success in forming the aggregates using the silver(I) oxide/thiourea methodology (compared to silver(I) sulfide) is the availability of solubilised silver(I) ions in the form of thiourea–silver adducts. Systems of this type have been reported previously [44], and attempts at deprotonation with base resulted in their decomposition to silver(I) sulfide, i.e. thiourea desulfurisation. Analogous reactions could conceivably occur at the gold(III) metal centre, which is more electronegative than platinum(II).

Since the uncomplexed Au–S–Au–S ring system could potentially provide a rich source of sulfide-bridged metal aggregates, we endeavoured to separate the Au_2S_2 monomer units from the silver–halide aggregates. Attempted abstraction/extrusion of silver from **4a** using sodium thiosulfate led only to decomposition of the complex to multiple compounds. Attempts at direct synthesis of a monomer by the reaction of the dichloride complex **3a** with sodium sulfide (the standard preparation for the platinum(II) sulfide complexes [45]), did not afford the gold-sulfide monomer $[\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Au(\mu\text{-}S)]_2$, but resulted only in a plethora of decomposition products, observed by NMR.

Finally, a preliminary investigation into the potential synthesis of gold-selenide bridged derivatives analogous to **4a** was undertaken. When *N*,*N*′-diphenylselenourea was refluxed with **3a** in the presence of silver(I) oxide, a wide range of compounds were detected, none of which correlated with a selenium analogue (or even a fragment) of **4a**. Interestingly, when *N*,*N*′-diphenylselenourea was reacted with *cis*-$[PtCl_2(PPh_3)_2]$ and silver(I) oxide in manner analogous to the preparation of **1d**, no selenium metallacycle analogous to **1a** formed, with ^{31}P-NMR showing the presence of at least seven compounds, including appreciable quantities of triphenylphosphine oxide, indicative of decomposition.

2.7. Conclusions

We have synthesised unusual gold-sulfido-silver-halide aggregates by an unanticipated thiourea desulfurisation reaction; related desulfurisation reactions using other transition metal (or main group) metal complexes might also provide new routes to heterobimetallic sulfido aggregates. Despite the ready formation of gold(III) metallacycles analogous to those formed by platinum(II) that we have previously reported [10,11], this work clearly demonstrates that the metallacyclic chemistry of gold(III) can nonetheless be significantly different and unpredictable, and further investigations will be reported in due course.

3. Experimental

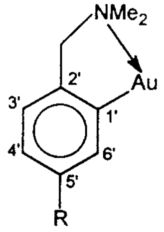
Melting points were measured in air on a Reichert hotstage apparatus and are uncorrected. Infrared spectra were recorded as KBr discs on a BioRad FTS-40 spectrophotometer. Electrospray mass spectra were recorded in positive-ion mode on a VG Platform II instrument, using methanol as the mobile phase. A range of cone voltages were used, in order to investigate the stability and formation of fragment ions of the parent aggregates. The ESMS data are presented in Table 3. Theoretical isotope patterns were calculated using the Isotope program [46].

Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Since the nature of the anion could not be determined and may well vary from preparation to preparation, the analysis results and calculated requirements should be taken as indicative only. For the theoretical calculations for the complexes **4a** and **4c** the counter-ions $[AgCl_3]^{2-}$ and $[AgBr_3]^{2-}$ have been assumed (based on X-ray data), and for **4b** and **4d** Cl^- and Br^- have been arbitrarily used.

All inverse 2D NMR experiments were recorded on a Bruker DRX 400 spectrometer at 400.13 and 100.61 MHz for the proton and carbon channels respectively, with $SiMe_4$ (0.0 ppm) as the standard. The proton and carbon NMR spectra were recorded on either the instrument above, or on a Bruker AC300 spectrometer at 300.13 and 75.47 MHz, respectively. All NMR analyses were carried out in $CDCl_3$.

All syntheses were carried out under a dry, oxygen-free, nitrogen atmosphere, in dark conditions, using solvents which were dried and freshly distilled prior to use. Once isolated, the gold-silver aggregates were air- and light-stable. The compounds $[Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl_2]$ [8] **3a** and $[Au\{C_6H_3(CH_2NMe_2)\text{-}2\}Cl_2]$ [9] **3b** were prepared as reported, by transmetallation of the respective orthomercurated complexes $[Hg\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl]$ [47] and $[Hg\{C_6H_4(CH_2NMe_2)\text{-}2\}Cl]$ [48] with Me_4NAuCl_4. *N*,*N*′-dimethylthiourea was prepared by reacting excess methylamine (33% in ethanol) with methyl isothiocyanate [49], and its purity checked by NMR [^{1}H-NMR: δ 6.61 (2H, s, N$\underline{H}$), 2.84 (6H, d, $^3J_{H,H} = 4.42$ Hz, C$\underline{H}_3$); ^{13}C-NMR: δ 182.1 (s, $\underline{C}$=S), 30.6 (q, CH$_3$)]. Silver(I) oxide and silver(I) sulfide were precipitated from the reactions of aqueous silver(I) nitrate with sodium hydroxide and sodium sulfide respectively. *N*,*N*′-diphenylselenourea was prepared by the literature procedure [50] from the reaction of phenyl isocyanide, elemental selenium and aniline, and its purity checked by NMR [m.p. 175–178°C; ^{1}H-NMR: (D$_6$-DMSO) δ 10.22 (2H, s, br, N$\underline{H}$), 7.49 (4H, d, $^3J_{2',3'} = 8.01$ Hz, H-2′,6′), 7.42 (4H, t, $^3J_{3',2'} = 7.74$ Hz, H-3′,5′), 7.48 (2H, t, $^3J4',3' = 7.20$ Hz, H-4′); ^{13}C-NMR: (D$_6$-DMSO) δ 178.6 (s, C=Se), 139.7 (s, C-1′), 128.5 (d, C-2′,6′), 125.2 (d, C-4′), 124.6 (d, C-3′,5′)]. *N*,*N*′-diphenylthiourea (BDH) was used as supplied.

3.1. General NMR numbering scheme



Scheme 1.

3.2. Preparation of **3c** and **3d**

These were prepared using a modification of the method previously described for the synthesis of **3d** [9]. To a flask containing **3a** (0.130 g, 0.301 mmol) or **3b** (0.120 g, 0.298 mmol) dissolved in acetone (20 ml), was added lithium bromide (0.2 g, excess) and the mixture stirred at r.t. for 2 h. The acetone was removed under reduced pressure, and the residue extracted with dichloromethane. After filtration to remove the insoluble lithium salts, addition of ether precipitated pure **3c** (0.118 g, 75%) or **3d** (0.120 g, 82%) as yellow powders.

3c: Found: C, 22.4; H, 2.7; N, 2.5%; $C_{10}H_{14}NOBr_2Au$ requires: C, 23.1; H, 2.7; N, 2.7%. **3d**: Found: C, 22.2; H, 2.5; N, 2.8%; $C_9H_{12}NBr_2Au$ requires: C, 22.0; H, 2.5; N, 2.9%. **3c**: ^{1}H-NMR: δ 7.58 (1H, d, $^4J_{6',4'} = 2.17$ Hz, H-6′), 7.78 (1H, d, $^3J_{3',4'} = 7.78$ Hz, H-3′), 7.79 (1H, dd, $^3J_{4',3'} = 8.34$ Hz, $4J_{4',6'} = 2.12$ Hz, H-4′), 4.34 (2H, s, C$\underline{H}_2$), 3.81 (3H, s, OC$\underline{H}_3$), 3.29 (6H, s, NC$\underline{H}_3$). ^{13}C-NMR: δ 158.0 (s, C-5′), 150.8 (s, C-1′), 136.2 (s, C-2′), 123.8 (d, C-6′), 118.2 (d, C-4′), 114.8 (d, C-3′), 75.3 (t, N$\underline{C}$H$_2$), 55.6 (t, OCH$_3$), 54.0 (q, N$\underline{C}$H$_3$). **3d**: ^{1}H-NMR: δ 7.98 (1H, d, $^3J_{6',5'} = 8.33$ Hz, H-6′), 7.26 (1H, t, $^3J_{4',3'} = 7.34$ Hz, H-4′), 7.14 (1H, d, $^3J_{3',4'} = 7.11$ Hz, H-3′), 7.10 (1H, t, $^3J_{5',6'} = 7.25$ Hz, H-5′), 4.40 (2H, s, C$\underline{H}_2$), 3.31 (6H, s, NC$\underline{H}_3$). ^{13}C-NMR: δ 150.4 (s, C-1′), 144.4 (s, C-2′), 133.4 (d, C-6′), 128.8 (d, C-4′), 128.3 (d, C-5′), 123.3 (d, C-3′), 75.7 (t, N$\underline{C}$H$_2$), 54.1 (q, N$\underline{C}$H$_3$).

3.3. Preparation of **4a**

To a nitrogen-flushed Schlenk flask containing dichloromethane (30 cm^3) was added $[\overline{Au\{C_6H_3(CH_2N}Me_2)\text{-}2\text{-}(OMe)\text{-}5\}Cl_2]$ **3a** (0.050 g, 0.116 mmol), *N*,*N*′-dimethylthiourea (0.013 g, 0.125 mmol), and silver(I) oxide (0.18 g, excess). The resulting mixture was stirred under reflux for 4 h. Without further precautions to exclude air or light, the insoluble silver salts were filtered off, and the supernatant evaporated to dryness to give a yellow oil. This was recrystallised by liquid–liquid diffusion of benzene layered on dichloromethane at 4°C to give bright yellow crystals of **4a** (0.032 g, 60%).

Alternatively, **3a** (0.050 g, 0.116 mmol) and silver(I) sulfide (0.15 g, excess) were refluxed in dichloromethane (30 ml) under nitrogen for 28 h. Analysis of the crude reaction mixture by ^{1}H- and ^{13}C-NMR and ESMS indicated the presence of at least five compounds. Repeated recrystallisation from dichloromethane-benzene, eventually led to the isolation of the gold aggregate **4a** (0.011 g, 20%), characterised by identical NMR and ESMS spectra with an authentic sample of **4a**.

M.p. 155–157°C. Found: C, 25.3; H, 3.1; N, 2.9; S, 6.5; Cl 4.9%; $[C_{60}H_{84}N_6O_6S_6Au_6Cl_2Ag_3]_{\frac{1}{2}}AgCl_3$ requires: C, 25.2; H, 3.0; N, 3.0; S, 6.7; Cl, 4.3%. ^{1}H-NMR: δ 7.16 (6H, d, $^3J_{3',4'} = 8.23$ Hz, H-3′), 7.00 (6H, d, $^4J_{6',4'} = 2.49$ Hz, H-6′), 6.68 (6H, dd, $^3J_{4',3'} = 8.21$ Hz, $^4J_{4',6'} = 2.57$ Hz, H-4′), 4.41 (6H, d, $^2J_{HB,HA} = 13.22$ Hz, NCH_B), 3.84 (18H, s, $OC\underline{H}_3$), 3.68 (6H, d, $^2J_{HA,HB} = 13.50$ Hz, $NC\underline{H}_A$), 2.73 (18H, s, $NC\underline{H}_{3B}$), 2.29 (18H, s, $NC\underline{H}_{3A}$). ^{13}C-NMR: δ 160.6 (s, C-5′), 157.6 (s, C-1′), 137.9 (s, C-2′), 124.8 (d, C-6′), 112.9 (d, C-4′), 112.2 (d, C-3′), 72.4 (t, $N\underline{C}H_2$), 55.7 (q, $O\underline{C}H_3$), 50.5 (q, NCH_{3B}), 49.4 (q, NCH_{3A}).

3.4. Preparation of **4b**

In an analogous preparation to that of **4a**, $[\overline{Au\{C_6H_4(CH_2N}Me_2)\text{-}2\}Cl_2]$ **3b** (0.050 g, 0.124 mmol), *N*,*N*′-dimethylthiourea (0.013 g, 0.125 mmol), and silver(I) oxide (0.15 g, excess) were reacted for 4 h. Subsequent work-up and recrystallisation from dichloromethane-ether, yielded **4b** as small yellow tetragonal shaped crystals (0.031 g, 57%).

M.p. 157–159°C. Found: C, 24.0; H, 2.9; N, 3.3%; $[C_{54}H_{72}N_6S_6Au_6Cl_2Ag_3]Cl$ requires: C, 24.9; H, 2.8; N, 3.2%. ^{1}H-NMR: δ 7.36 (6H, d, $^3J_{6',5'} = 8.00$ Hz, H-6′), 7.27 (6H, d, $^3J_{3',4'} = 6.11$ Hz, H-3′), 7.16 (6H, t, $^3J_{4',3'} = 7.19$ Hz, H-4′), 7.08 (6H, t, $^3J_{5',4'} = 6.53$ Hz, H-5′), 4.43 (6H, d, $^2J_{HB,HA} = 13.50$ Hz, NCH_B), 3.54 (6H, d, $^2J_{HA,HB} = 13.71$ Hz, $NC\underline{H}_A$), 2.61 (18H, s, NCH3B), 2.17 (18H, s, NCH3A). ^{13}C-NMR: δ 160.1 (s, C-1′), 145.7 (s, C-2′), 128.8 (d, C-6′), 127.4 (d, C-4′), 127.1 (d, C-5′), 124.3 (d, C-3′), 73.1 (t, $N\underline{C}H_2$), 50.0 (q, NCH_{3B}), 48.4 (q, NCH_{3A}).

3.5. Preparation of **4c**

In an analogous preparation to that of **4a**, $[Au\{C_6H_3(CH_2NMe_2)\text{-}2\text{-}(OMe)\text{-}5\}Br_2]$ **3c** (0.065 g, 0.125 mmol), *N*,*N*′-dimethylthiourea (0.014 g, 0.134 mmol), and silver(I) oxide (0.13 g, excess) were reacted for 4 h. Recrystallisation from dichloromethane-ether yielded **4c** as thin yellow plates (0.040 g, 53%).

M.p. 178–180°C. Found: C, 23.3; H, 2.9; N, 2.9%; $[C_{60}H_{84}N_6O_6S_6Au_6Br_2Ag_3]_{\frac{1}{2}}AgBr_3$ requires: C, 24.2; H, 2.9; N, 2.8%. ^{1}H-NMR: δ 7.23 (6H, d, $^3J_{3',4'} = 8.19$ Hz, H-3′), 6.98 (6H, d, $^4J_{6',4'} = 2.40$ Hz, H-6′), 6.71 (6H, dd, $^3J_{4',3'} = 8.05$ Hz, $^4J_{4',6'} = 2.28$ Hz, H-4′), 4.43 (6H, d, $^2J_{HB,HA} = 14.60$ Hz, NCH_B), 3.82 (18H, s, $OC\underline{H}_3$), 3.51 (6H, d, $^2J_{HA,HB} = 13.31$ Hz, $NC\underline{H}_A$), 2.68 (18H, s, $NC\underline{H}_{3B}$), 2.29 (18H, s, $NC\underline{H}_{3A}$). ^{13}C-NMR: δ 160.6 (s, C-5′), 157.5 (s, C-1′), 137.7 (s, C-2′), 124.8 (d, C-6′), 112.7 (d, C-4′), 112.1 (d, C-3′), 72.3 (t, $N\underline{C}H_2$), 55.8 (q, $O\underline{C}H_3$), 50.6 (q, NCH_{3B}), 49.1 (q, NCH_{3A}).

3.6. Preparation of **4d**

In an preparation analogous to that of **4a**, $[\overline{Au\{C_6H_4(CH_2N}Me_2)\text{-}2\}Br_2]$ **3d** (0.060 g, 0.122 mmol), *N*,*N*′-dimethylthiourea (0.013 g, 0.125 mmol), and silver(I) oxide (0.21 g, excess) were reacted for 3 h. Subsequent work-up and recrystallisation from dichloromethane-benzene yielded **4d** as small yellow rectangular blocks (0.029 g, 52%).

M.p. 167–169°C. Found: C, 22.6; H, 2.6; N, 3.2%; $[C_{54}H_{72}N_6S_6Au_6Br_2Ag_3]Br$ requires: C, 23.7; H, 2.7; N, 3.1%. ^{1}H-NMR: δ 7.40 (6H, d, $^3J_{6',5'} = 7.53$ Hz, H-6′), 7.25 (6H, d, $^3J_{3',4'} = 8.30$ Hz, H-3′), 7.17 (6H, t, $^3J_{4',3'} = 6.73$ Hz, H-4′), 7.09 (6H, t, $^3J_{5',4'} = 7.16$ Hz, H-5′), 4.49 (6H, d, $^2J_{HB,HA} = 13.55$ Hz, NCH_B), 3.55 (6H, d, $^2J_{HA,HB} = 14.22$ Hz, $NC\underline{H}_A$), 2.68 (18H, s, $NC\underline{H}_{3B}$), 2.24 (18H, s, $NC\underline{H}_{3A}$). ^{13}C-NMR: δ 159.9 (s, C-1′), 145.6 (s, C-2′), 128.5 (d, C-6′), 127.3 (d, C-4′), 126.9 (d, C-5′), 124.3 (d, C-3′), 73.1 (t, $N\underline{C}H_2$), 50.2 (q, NCH_{3B}), 48.4 (q, NCH_{3A}).

3.7. Preparation of **1d**

To a flask containing dichloromethane (30 ml) was added *cis*-$[PtCl_2(PPh_3)_2]$ (0.102 g, 0.129 mmol), *N*,*N*′-dimethylthiourea (0.014 g, 0.134 mmol) and silver(I) oxide (0.12 g, excess), and the solution refluxed for 4 h. The silver salts were filtered off, giving a bright yellow solution. The dichloromethane was removed under reduced pressure to leave a residue which was slowly recrystallised by vapour diffusion of diethyl ether into a dichloromethane solution, to give bright yellow crystals of **1d** (0.080 g, 75%). Found: C, 55.6; H, 4.2; N, 3.3%. $C_{39}H_{36}N_2SP_2Pt \cdot \frac{1}{2}CH_2Cl_2$ requires: C, 54.9; H, 4.3; N, 3.2%. ESMS: (Cone voltage = 20 V) *m*/*z* 823 ($[MH]^+$, 100%). (Cone voltage = 50 V) m/z 823 ([MH]$^+$, 100%). (Cone voltage = 80 V) m/z 823 ([MH]$^+$, 100%), 759 ($[\overline{\text{Pt}\{\text{C}_6\text{H}_4\text{P}}\text{Ph}_2\}(\text{PPh}_3)+\text{MeCN}]^+$, 33%), 718 ($[\overline{\text{Pt}\{\text{C}_6\text{H}_4\text{P}}\text{Ph}_2\}(\text{PPh}_3)]^+$, 17%).

^{31}P-NMR: δ 17.0 (d, $^2J_{\text{P,P}} = 21.2$ Hz, (d, $^1J_{\text{P,Pt}} = 3216.8$ Hz), PPh$_3$ *trans* S), 12.3 (d, $^2J_{\text{P,P}} = 21.2$ Hz, (d, $^1J_{\text{P,Pt}} = 3304.7$ Hz), PPh$_3$ *trans* N). ^{1}H-NMR: δ 7.45-7.15 (30H, m, PPh$_3$), 5.28 (1H, s, C$\underline{\text{H}}_2$Cl$_2$), 2.76 (3H, s, C=NC$\underline{\text{H}}_3$), 2.27 (3H, s, (d, $^4J_{\text{H,P}} = 4.29$ Hz, (d, $^1J_{\text{P,Pt}} = 31.21$ Hz), PtNC$\underline{\text{H}}_3$). ^{13}C-NMR: δ 177.0 (s, (d, $^3J_{\text{C,P}} = 8.72$ Hz), $\underline{\text{C}}$=N), 134.4 (d, (d, $^3J_{\text{C,P}} = 11.70$ Hz), C-3,5 PPh$_3$), 133.8 (d, (d, $^3J_{\text{C,P}} = 11.17$ Hz), C-3,5 PPh$_3$), 131.8 (d, (d, $^4J_{\text{C,P}} = 2.19$ Hz), C-4 PPh$_3$), 131.5 (d, (d, $^4J_{\text{C,P}} = 2.11$ Hz), C-4 PPh$_3$), 128.8 (d, (d, $^2J_{\text{C,P}} = 11.09$ Hz), C-2,6 PPh$_3$), 128.6 (s, (d, $^2J_{\text{C,P}} = 11.32$ Hz), C-2,6 PPh$_3$), 36.4 (q, (d, $^3J_{\text{C,P}} = 7.55$ Hz), PtN$\underline{\text{C}}$H$_3$), 26.5 (q, C=N$\underline{\text{C}}$H$_3$).

4. X-ray crystal structures

Unit cell dimensions and intensity data for both the structures were obtained on a Siemens CCD SMART diffractometer at 203(2) K, with monochromatic Mo–K$_\alpha$ X-rays ($\lambda = 0.71073$ Å), at the University of Auckland. The data collections nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω. The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS [51]. Details for each study follows.

4.1. X-ray structure determination of **4a**

Collection data: total reflections = 195914, unique reflections = 7500, range = $0.73 < \theta < 23.25°$, absorption correction $T_{\text{max., min.}} = 0.55$, 0.34.

Crystal data: $\text{C}_{60}\text{H}_{74}\text{N}_6\text{O}_6\text{S}_6\text{Cl}_{2.83}\text{Ag}_{3.33}\text{Au}_6$, $M_r = 2809.42$, cubic, space group $Pn-3n$, $a = b = c = 39.6709(4)$ Å, $U = 62433.3(11)$ Å^3, $D_{\text{calc}} = 1.793$ g cm^{-3}, $Z = 24$, $F(000) = 31172$, $\mu(\text{Mo–K}_\alpha) = 9.265$ mm^{-1}.

Solution and refinement: The structure was solved by the Patterson methods option of SHELXS-96 [52], to give the gold atom positions. All further non-hydrogen atoms were located routinely (SHELXL-96 [53]) in subsequent difference maps. During full-matrix least-squares refinements based on F^2, all non-hydrogen atoms were eventually assigned anisotropic temperature factors. All aromatic rings were modelled as rigid hexagons (bond distances 1.390 Å, bond angles 120°), with the carbon atoms attached to gold providing the pivot points. Hydrogen atoms were not included in the model. The anion was modelled as [AgCl$_3$]$^{2-}$, with site occupancy of 0.66 for overall neutrality. One of the methoxy groups [that bound to C(15)] was found to be disordered over two locations, each with half occupancy, and these have been denoted C(10A) and C(10B). The refinement converged with $R_1 = 0.0693$ for 5231 data with $I \geq 2\sigma(I)$, 0.1141 for all data; $wR_2 = 0.2189$ $\{w = 1/[\sigma^2(F_o^2) + (0.0891P)^2 + 2105.2412P]$ where $P = (F_o^2 + 2F_c^2)/3\}$, and GOF = 1.160. No parameter shifted in the final cycle. The final difference map showed no peaks or troughs of electron density > 2.747 and 1.215 e Å^{-3}, respectively, both adjacent to gold atoms.

4.2. X-ray structure determination of **4d**

Collection data: crystal dimensions $0.52 \times 0.20 \times 0.08$ mn, total reflections = 56055, unique reflections = 30904, range = $0.95 < \theta < 26.54°$, absorption correction $T_{\text{max., min.}} = 0.48$, 0.27.

Crystal data: $\text{C}_{54}\text{H}_{72}\text{N}_6\text{S}_6\text{Br}_2\text{Ag}_3\text{Au}_6$ excluding anion, $M_r = 2662.77$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.1201(2)$, $b = 21.5804(2)$, $c = 32.6181(2)$ Å, $\alpha = 88.724(1)$, $\beta = 79.717(1)$, $\gamma = 82.704(1)°$, $U = 8326.48(17)$ Å^3, $D_{\text{calc}} = 2.124$ g cm^{-3}, $Z = 4$, $F(000) = 4876$, $\mu(\text{Mo–K}_\alpha) = 12.358$ mm^{-1}.

Solution and refinement: The structure was solved by the Patterson methods option of SHELXS-96 [52]. All further non-hydrogen atoms were located routinely (SHELXL-96 [53]). During full-matrix least-squares refinements based on F^2, all non-hydrogen atoms were eventually assigned anisotropic temperature factors. All aromatic rings were modelled as rigid hexagons (bond distances 1.390 Å, bond angles 120°), with the carbon atoms attached to gold providing the pivot points. Hydrogen atoms were not included in the model. The refinement converged with $R_1 = 0.1090$ for 17991 data with $I \geq 2\sigma(I)$, 0.1706 for all data; $wR_2 = 0.3060$ $\{w = 1/[\sigma^2(F_o^2) + (0.1420P)^2 + 334.4861P]$ where $P = (F_o^2 + 2F_c^2)/3\}$, and GOF = 1.029. No parameter shifted in the final cycle. The final difference map showed a number of large peaks of electron density (maximum 7.11 e Å^{-3}) all of which were in close proximity to silver atoms, presumably the result of some disorder. These could not be modelled satisfactorily. The largest trough of electron density (-3.25 e Å^{-3}) is adjacent to Au(15). The anions required for charge neutrality could not be located (see text).

Atomic coordinates, full bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation.

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