Secondary Interactions in Gold(I) Complexes with Thione Ligands. 2. Three Ionic Camphorsulfonates with *Z'* = 2 [1]

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Dedicated to Prof. Dr. Reinhard Schmutzler on the occasion of his 70th birthday

All three structures of the form bis(thione)gold(I) camphor-10-sulfonate [thione = imidazolidine-2-thione, **1**; 1-methyl-imidazolidine-2-thione, **2**; thiazolidine-2-thione, **3**] crystallize in chiral space groups with $Z' = 2$; local inversion symmetry of the cationic assemblies (less pronounced for **3**) provides some rationalisation for this. The basic structural units are accounted for in terms of classical hydrogen bonds, leading to rings involving ion pairs for **1** and **2**, but to infinite chains of anions and cations for **3**. Neighbouring ion pairs in **1** are joined by further classical hydrogen bonds, in **2** *via* interactions between parallel S-Au-S axes. Other interactions include Au···N for **1**, Au···S and Au···O for **3**, and weak hydrogen bonds C-H···O and C-H···S, especially between adjacent chains in **3**. Each structure is divided into hydrophobic and hydrophilic regions.

Key words: Aurophilicity, Thiones, Camphorsulfonate, Gold, Hydrogen Bonds

Introduction

We are interested in secondary interactions in gold(I) complexes and have recently extended our studies to gold(I) complexes involving heterocyclic ligands bearing a thione group. The first publication [1], which may be consulted for further introductory material, presented structures of the cations $[L_2Au]^+$, with L = imidazolidine-2-thione ("ethylenethiourea", etu) and 1-methyl-imidazolidine-2-thione (Me-etu), as their chloride salts. Here we have used camphor-10-sulfonate, henceforth abbreviated as Q^-, as the counteranion; it is completely different from chloride in its size, nature (hydrophilic and hydrophobic regions) and enantiomeric purity, and would thus be expected to promote correspondingly different packing motifs. We have determined three structures, namely $[L_2Au]^+Q^-$ with L = etu (**1**), Me-etu (**2**) and thiazolidine-2-thione (tzt) (**3**).

Discussion

General aspects

Because of the chiral anion, the compounds necessarily crystallize in chiral space groups. Unusually, all three compounds crystallize with two formula units in the asymmetric unit ($Z' = 2$; Figs 1 – 3). Compound (**2**) crystallizes additionally with one molecule of acetonitrile and one molecule of methanol (Fig. 2); for a more valid comparison of the three structures, a solvent-free form would have been preferred, but could not be obtained as single crystals. The reasons for the formation of structures with $Z' > 1$ are not well understood, despite a recent attempt at classification and rationalisation [2], and, as recently commented [3], the phenomenon is currently impossible to predict.

All complexes show a similar moderate distortion of the S-Au-S bond angles from linearity, with all values close to 172°. Bond lengths and angles may be considered normal, *e.g.* the Au-S bond lengths, which lie in the range 2.269 – 2.293 Å, or the C-S bond lengths, which are *ca.* 1.7 Å at the urea-type carbons but approximately 0.1 Å longer for the CH_2 carbons of the tzt ligand in **3**; for individual values, Tables 2 – 4 or the Supplementary Material should be consulted.

Our previous publication [1] established that the most relevant structural degree of freedom in the cations is the torsion angle C-S···S-C (combined, for the asymmetric thiourea ligands tzt and Me-etu, with the "inward" or "outward" direction of the NH

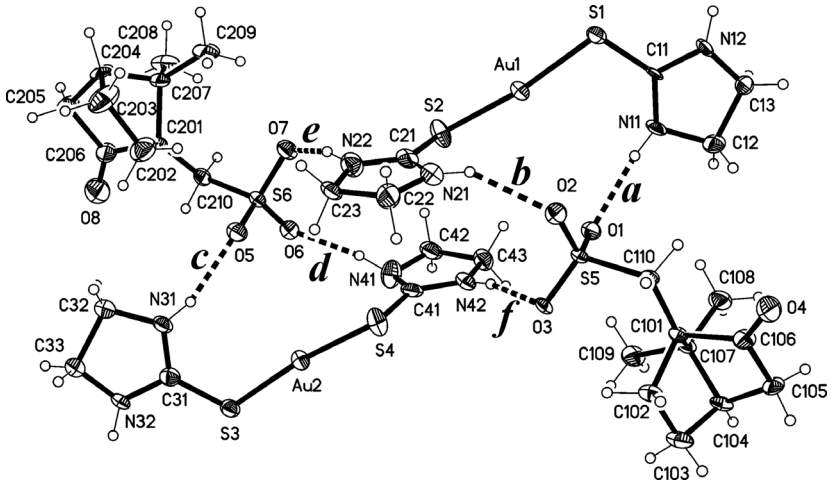

Fig. 1. Bis(imidazolidine-2-thione) gold(I) camphor-10-sulfonate, **1**, asymmetric unit with numbering scheme. Displacement ellipsoids are shown with 50% probability. Hydrogen radii are arbitrary. Dashed lines represent hydrogen bonds, labelled with italic letters, corresponding to Table 5.

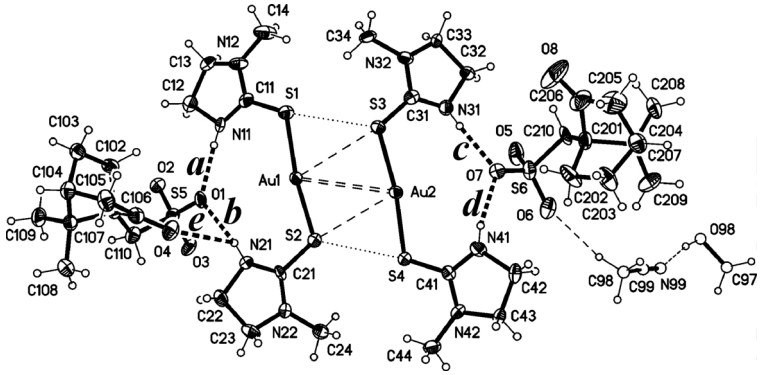

Fig. 2. Bis(1-methyl-imidazolidine-2-thione)gold(I) camphor-10-sulfonate $\cdot 1/2$ CH_3CN $\cdot 1/2$ CH_3OH, **2**, asymmetric unit with numbering scheme. Displacement ellipsoids are shown with 50% probability. Solvent and hydrogen radii are arbitrary. Dashed and dotted lines represent secondary contacts (hydrogen bonds, Au···Au, Au···S and S···S interactions). Hydrogen bonds are labelled with italic letters, corresponding to Table 6.

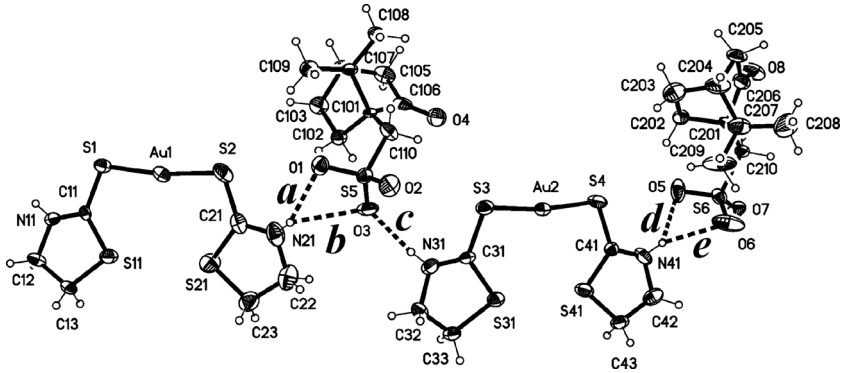

Fig. 3. Bis(1,3-thiazolidine-2-thione)gold(I) camphor-10-sulfonate, **3**, asymmetric unit with numbering scheme. Displacement ellipsoids are shown with 50% probability. Hydrogen radii are arbitrary. Dashed lines represent hydrogen bonds, labelled with italic letters, corresponding to Table 7. The chain is extended by the interaction N11-H11···O7#1.

groups). The complex cations in **1** and **2** show related staggered conformations [torsion angles 111.4(5)°, −111.1(5)° (**1**) and −71.9(4)°, 70.3(4)° (**2**)], whereas in **3**, the heterocyclic ligand rings are arranged parallel and eclipsed, with torsion angles 9.1(4)° and −9.8(4)°. There is little or no similarity to values for the same cations in [1], and we note that this makes effective planning of the crystal packing ("crystal engineering") at best a difficult exercise. All the heterocyclic rings are approximately planar (mean deviations < 0.1 Å) and the gold atoms are approximately coplanar with the rings (mean absolute Au-S-C-N or Au-S-C-S torsion angles are 21°, 15°, 8° respectively for **1**, **2** and **3**).

In contrast to many gold(I) species, which display short "aurophilic contacts" between formally non-bonded, two-coordinate gold atoms, compound **1** has a

shortest Au···Au distance of 6.32 Å and **3** of 5.52 Å (for compound **2**, see below).

Crystal packing: classical hydrogen bonds lead to "dimeric" units or chains

The main interest in these structures was, however, to determine their crystal packing. It is to the first aspect of this, the classical hydrogen bonds, that we now turn. All such hydrogen bonds in **2**, and all except those from N12 and N32 in **1**, are contained within the respective asymmetric units (Figs 1 and 2). One structural motif is reminiscent of the $[(etu)_2Au]^+$ Cl^- structures [1], in which two NH donors of the cation formed hydrogen bonds to the same acceptor (chloride or water) to give ten-membered rings of graph set $R_2^1(10)$; in **1** and **2** similar rings are formed, in which the sulfonate group assumes the acceptor role, but in different ways. For each ion pair of **1** (Fig. 1), two N-H···O bonds are formed between the two inward directed NH groups (N11,N21) and (N31,N41) and two different oxygen atoms of the respective sulfonate group (O1,O2) and (O5,O6), to give a larger ring pattern, which, at the binary level, can be described as $N_2(a,b) \equiv N_2(c,d)$: $R_2^2(12)$. The ion pairs are then mutually linked by the hydrogen bonds *e* [N22-H22···O7] and *f* [N42-H42···O3], completing the structural unit of two cations and two anions *via* the formation of a ring structure at the quaternary level [$N_4(b,d,e,f)$: $R_4^4(16)$]; we loosely refer to such groupings as "dimers" in the following discussion. A short intraannular Au···O contact [Au2···O5 3.464(6) Å] is observed. It is noteworthy that the cations and the sulfonate groups (without the camphor substituents!) form an almost inversion-symmetric region of the structure, with the pseudo-inversion centre at *ca.* 0.25, 0.212, 0.25; the r.m.s. deviation of a least-squares fit of both inversion-related halves was only 0.16 Å (without the oxygens, 0.08 Å). With hindsight, the tendency to form a centrosymmetric substructure may here be regarded as a factor contributing to the formation of a structure with $Z' = 2$.

In **2** (Fig. 2), the ion pairs are both formed by bifurcated hydrogen bonds (hydrogen bond acceptors O1, O7) to give the previously observed [1], smaller ring pattern $R_2^1(10)$ on the binary level [$N_2(a,b) \equiv N_2(c,d)$]. In contrast, the chloride salts with the Me-etu [1] and ^{i}Pr-etu ligands [4] did not form any such rings, adopting instead an antiperiplanar geometry of the C-S···S-C moiety. Again, short intraannular Au···O contacts [Au1···O1 3.369(5) and Au2···O7 3.464(6) Å] are observed. A three-centre hydrogen bond from H21, with the binary graph set $N_2(b,e)$: $R_1^2(7)$, is completed by the weak contact to the carbonyl oxygen acceptor O4. There are no further classical hydrogen bond donors in **2**, and the two independent formula units of the "dimer" are linked instead by a striking series of contacts between the two parallel S-Au-S axes [S1···S3 3.599(3), S2···S4 3.554(3), Au1···Au2 3.7711(4), Au1···S3 3.878(2), Au2···S2 3.852(2) Å; the angle between the vectors S1-S2 and S3-S4 is 0.6°]. Again, the cation assembly is inversion-symmetric to a good approximation; the pseudo-inversion centre lies at 0.25, 0.446, 0.5 and the r.m.s. deviation for the mutual fit of the two cations plus O1/O7 is 0.08 Å.

The structure of compound **3** is completely different (Fig. 3); no "dimeric" units are formed. The rings in both cations display a *cis* conformation and are approximately parallel, with sulfur atoms facing each other in the centre, as in $[(tzt)_2Au]^+$ $Cl^-{\cdot}H_2O$ [5]; the intraionic S…S distances are 3.682(3) and 3.697(3) Å, and the 1,4-distances between gold and the ring sulfur atoms are 3.3–3.4 Å, over which distance weak bonding interactions have been proposed [5]. At the binary level, two ion pairs are formed *via* the three-centre hydrogen bonds (*a*,*b*) and (*d*,*e*), respectively connecting H21 and H41 with two oxygen atoms (O1,O3) and (O5,O6) of each sulfonate group to give the small ring pattern $N_2(a,b) \equiv N_2(d,e)$: $R_1^2(4)$. The two resulting ion pairs are connected within the asymmetric unit by the classical NH···O bonds *c* [N31-H31···O3], thereby engaging O3 in the formation of a bifurcated hydrogen bond; the hydrogen bond *f* [N11-H11···O7#1, by *z* translation] links the asymmetric units *via* outwardly extended NH donors to form a chain parallel to the *z* axis [$N_6(a,b,c,d,e,f)$: $C_4^4(24)$]. Again, approximate local inversion symmetry is present, not within the chain, but *via* the pseudo-inversion centre at *ca.* 0.8, 0.5, 0.125 to a neighbouring chain generated by the 2_1 screw axis parallel to *z*. The fit is not as good as for the other structures; the r.m.s. deviation is 0.13 Å for the atoms of the cations.

Crystal packing: further interactions

The extended packing for compound **1** involves primarily the two additional classical NH···O hydrogen bonds (donors H12 and H32). These link adjacent asymmetric units, related through the 2_1 axes, *via* the hydrogen bonds *g* [N12-H12···O2#1] and *h* [N32-

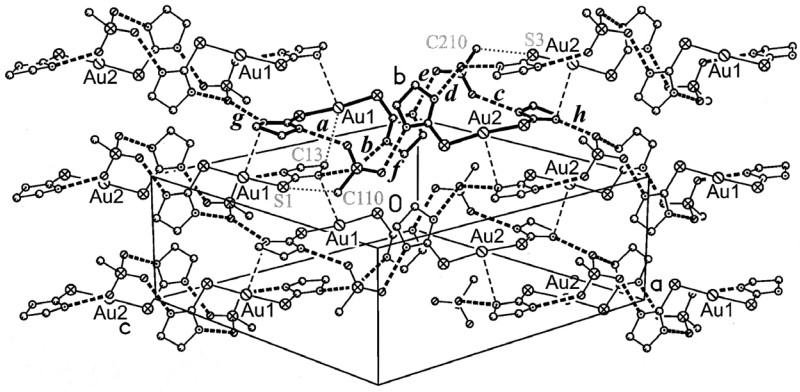

Fig. 4. Compound **1**, layer structure viewed perpendicular to (101). Dashed lines represent hydrogen bonds (thick) or Au···N interactions (thin). The asymmetric unit is accentuated by thicker bonds. Hydrogen atoms and anion carbons (except those bonded to sulphur) are omitted for clarity. One of each type of C-H···S and C-H···Au interaction is shown as grey dashed bonds; the participating atoms are labelled with grey letters.

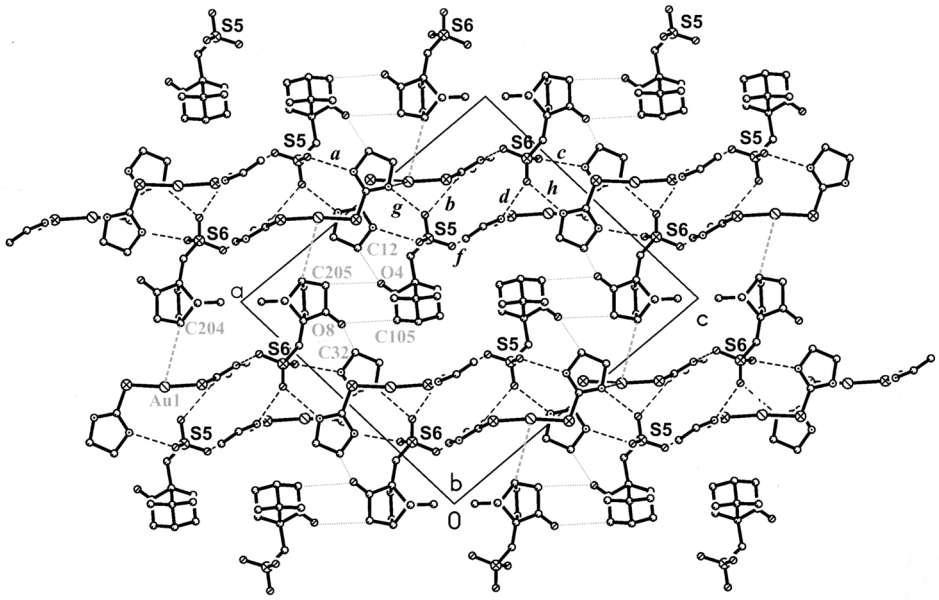

Fig. 5. Compound **1**, layer structure viewed from the side (projection onto the *y* axis). Thin dashed lines represent classical hydrogen bonds. In the left-hand corner of the cell, one set of C-H···O interactions involving the anions are shown as thick dashed bonds. Hydrogen atoms are omitted for clarity. C-H···Au and C-H···O interactions are shown as thick grey dashed bonds and thin grey dotted bonds, respectively; one of each set of the participating atoms are labelled with grey letters.

H32···O6#2] to form a layer structure perpendicular to (101) (Fig. 4). An additional feature of these layers are short Au···N contacts [Au1···N12 3.292(8), Au2···N32 3.295(9) Å] (Fig. 4).

All six oxygen atoms of the sulfonate SO_3 groups in **1** thus act as classical hydrogen bond acceptors. Further down the hierarchy of secondary interactions are the "weak" hydrogen bonds of the type C-H···X. For X = O, the ketone oxygens of the anions, O4 and O8, which are not involved in classical hydrogen bonding, each accept two weak hydrogen bonds. These interactions serve to link the anions in pairs and also to connect adjacent asymmetric units parallel to the *y* axis (Fig. 5), forming layers of a more hydrophobic nature between the cations. The sterically exposed nature of the cation Au and S atoms makes them available as acceptors for the following secondary interactions: the contacts C110-H11A···S1 and C210-H21B···S3, both within the layer shown in Fig. 4, link the CH_2 groups *alpha* to the anion sulfurs; C13-H13B···Au1, also located within the same layer, links those rings with Au1···N interactions (see above); and C204-

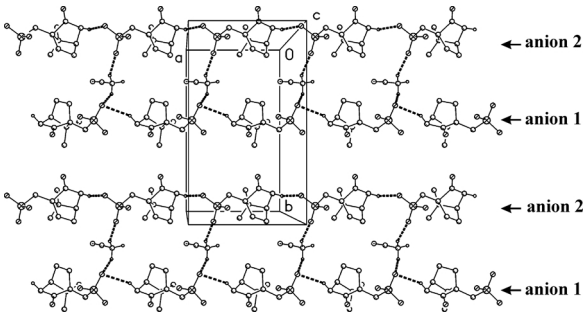

Fig. 6. Compound **2**, layer of anions and acetonitrile at $z \approx 1/8$ viewed parallel to the *z* axis. Dashed lines represent C-H···O interactions. The four horizontal chains of anions involve the sulfur atoms S6, S5, S6, S5 respectively from top to bottom.

H204···Au1 links adjacent layers in Fig. 5. We ascribe less structural significance to these interactions, many of which are long enough to be considered borderline cases, and only one of each kind is included explicitly in the Figures.

For compound **2**, despite the fact that only three of the six SO_3 group oxygen atoms act as classical hydrogen bond acceptors, there are few significant C-H···O contacts between neighbouring dimers. The only unambiguous case is the weak hydrogen bond H33A···O4, which provides a link in the *x* direction (Fig. 6). Possible three-centred or bifurcated contacts involving the ketonic oxygen atoms [H22B···O4,O8] and one of the sulfonate oxygen atoms [H32A,H33B···O3] display extremely narrow angles at the hydrogens (101° – 117°), even allowing for the fact that narrower angles are more common in such systems.

Closer inspection of structure **2** reveals that the linkages are provided by the anions and the solvent molecules. Within the asymmetric unit, the acetonitrile acts as donor in the hydrogen bond to O6 and as acceptor to the hydrogen bond from the methanol molecule (Fig. 2). Viewed along the *z* axis (Fig. 6), layers of anions and acetonitrile molecules are assembled *via* four short C-H···O interactions. A side-on view of the complete structure (Fig. 7) shows that there are clearly distinguishable regions in the direction of the long *z* axis. Starting with the cation layer at $z \approx 1/2$, one progresses to layers of anions at $z \approx 7/8$, $9/8$, mediated by a solvent region at $z \approx 1$. The contact from the camphorsulfonate CH_3-group (C209) to the methanol oxygen acts as a further link between solvent and anion, while the oxygens O3 and O8 remain without involvement in hydrogen bonds of any type.

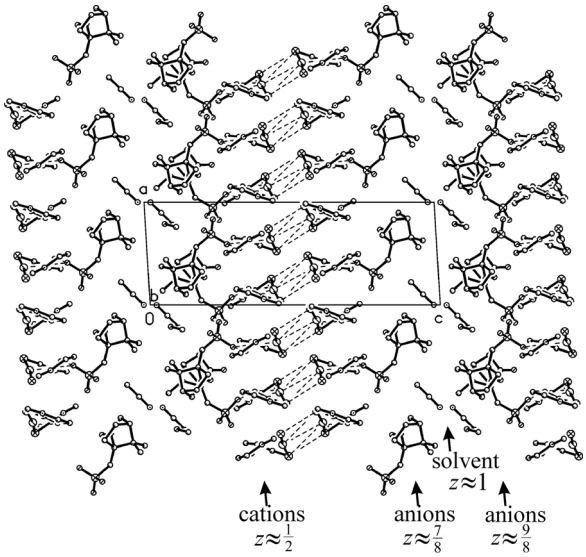

Fig. 7. Compound **2**, composite layer structure viewed from the side (projected parallel to the *y* axis). The cation region at $z \approx 1/2$ includes the secondary contacts between the two independent cations; other secondary contacts are not shown (see text).

There are also two C-H···Au and one C-H···S interactions, two of which (from H34B) form a three-centre system of acceptable linearity, but all are very long, and we do not discuss them further.

The packing of the chains of compound **3** involves a large number of secondary contacts. Fig. 8 shows the ten C-H···O interactions, including three bifurcated systems from neighbouring ring C-H donors, from the cationic chain residues to neighbouring anions. Some

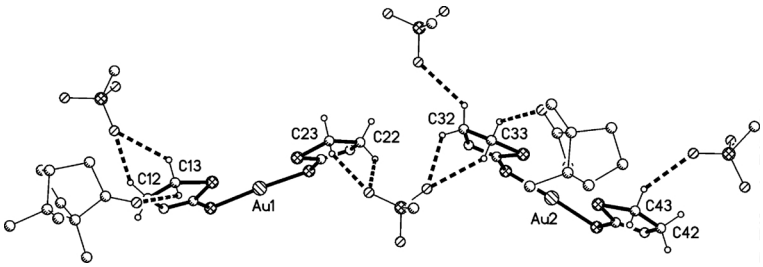

Fig. 8. Compound **3**, showing the C-H···O interactions (dashed bonds) with the donors of the two independent cations. For clarity, anions are reduced to SO_3C moieties unless the ketonic oxygen is involved.

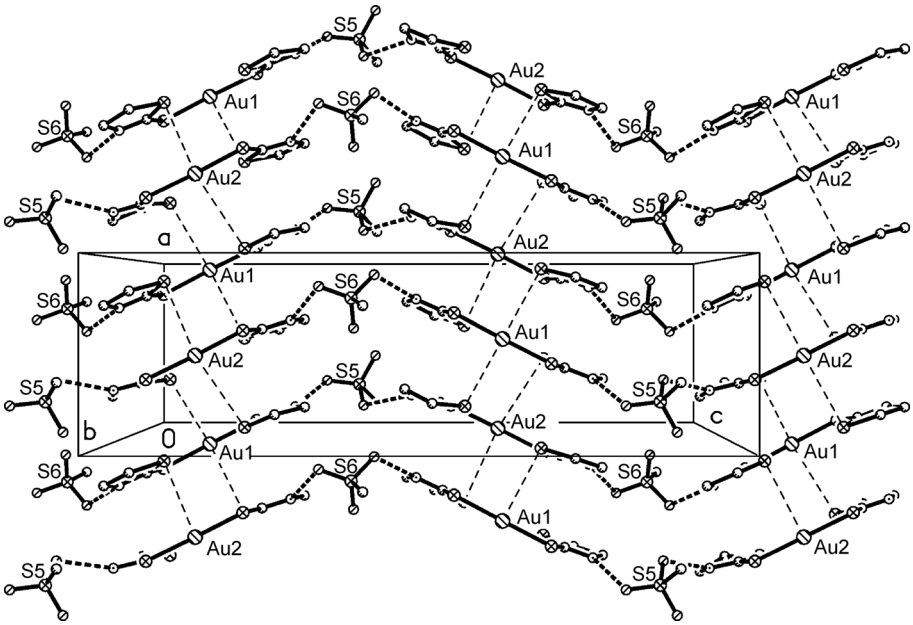

Fig. 9. Compound **3**, view parallel to the *y* axis of the region at $y \approx 1/2$, showing the Au···S contacts (dashed bonds). For clarity, anions are reduced to SO_3C moieties.

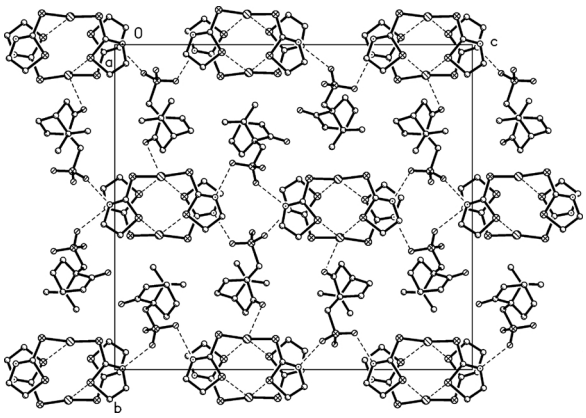

Fig. 10. Compound **3**, projection parallel to the *x* axis (chain direction), showing the secondary contacts (hydrogen bonds, Au···S and Au···O) as dashed bonds. Hydrogen atoms are omitted for clarity.

of the H···O distances are very short, although all the angles are markedly non-linear. Subjectively more striking, however, are the Au···S contacts between neighbouring chains in the *x* direction (Fig. 9), which are short for Au1 [···S31 3.502(2), ···S41 3.665(2) Å] and somewhat longer for Au2 [···S11 3.632(2), ···S21 3.920(2) Å]. The close stacking is also associated with several C-H···S interactions, one as short as 2.79 Å, and several rather long (> 3.19 Å) C-H···Au contacts. It is, however, not clear if these distances are the cause or the result of the chain stacking. The cationic moieties occupy the areas at $y \approx 0$, $1/2$, etc., with the camphor residues forming hydrophobic layers at $y \approx 1/4$, $3/4$, etc. Fig. 10 shows the layer structure and also the short contact Au1···O8, 3.296(6) Å. There is no hydrogen bonding between the anions.

Conclusions

The use of a large chiral counteranion changes the packing of the bis(thione)gold(I) cations markedly with respect to that of the chlorides, but not in an entirely predictable way. All three structures crystallize with $Z' = 2$, which may be rationalised in terms of local inversion symmetry of the cation assemblies, but could not have been foreseen. The amphiphilic nature of the anion leads to the formation of hydrophilic and hydrophobic regions of the structures. The flexibility of the cations, in which the C-S···S-C torsion angle can adopt virtually any value, precludes attempts at crystal engineering. In compound **1**, which has twice as many classical donors as **2** and **3**, the classical hydrogen bonds account for most features of the packing. In compound **2**, the classical hydrogen bond donors are used exhaustively in each formula unit, which are then connected by a striking association of two parallel S-Au-S axes; the anions and solvent provide further links *via* C-H···O interactions. The classically hydrogen-bonded chains of compound **3** are linked by a large number of C-H···O and C-H···S interactions.

Table 1. Crystallographic data collection, solution and refinement details for **1**, **2** and **3**.

Compound	**1**	**2** $^1/_2CH_3OH\cdot{}^1/_2CH_3CN$	**3**
Formula	$C_{16}H_{27}AuN_4O_4S_3$	$C_{39.5}H_{34.5}AuN_{4.5}O_{4.5}S_6$	$C_{16}H_{25}AuN_2O_4S_5$
M_r [g/mol]	632.56	697.16	666.65
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$
Cell dimensions [Å, °]	$a = 16.881(3)$	$a = 8.0741(8)$	$a = 7.5949(10)$ Å
	$b = 6.9434(10)$	$b = 13.8904(14)$	$b = 23.154(3)$ Å
	$c = 18.365(3)$	$c = 22.792(2)$	$c = 25.440(3)$ Å
	$\beta = 96.718(4)$	$\beta = 93.403(3)$	$\beta = 90$
V [Å^3]	2137.8(6)	2551.6(4)	4473.8(10)
Z	4	4	8
Crystal habit	colourless plate	colourless plate	colourless needle
Crystal size [mm^3]	$0.26 \times 0.08 \times 0.02$	$0.24 \times 0.13 \times 0.04$	$0.80 \times 0.08 \times 0.03$
D_x [Mg/m^3]	1.965	1.815	1.980
θ Range	1.12 to 29.99°	1.72 to 30.00°	1.60 to 28.32°
μ [mm^{-1}]	7.205	6.047	7.069
Temperature [K]	143	143	173
Absorption correction	multiple scans (SADABS)	multiple scans (SADABS)	multiple scans (SADABS)
T_{min}/T_{max}	0.962 / 0.406	0.999 / 0.691	0.999 / 0.472
Measured reflections	25533	30651	30658
Independent reflections	12246	14410	11034
R_{int}	0.059	0.040	0.068
$F(000)$	1240	1384	2608
Restraints	583	153	120
Parameters	527	584	521
Flack parameter	0.007(9)	0.015(6)	$-0.012(6)$
S	1.01	0.97	0.92
$R1[F^2 > 2\sigma(F^2)]$	0.0514	0.0358	0.0419
$wR2(F^2$, all refl.)	0.1187	0.0794	0.0752
$\Delta\rho_{min}/\Delta\rho_{max}$ [eÅ^{-3}]	3.198 / -4.659	2.061 / -1.558	1.072 / -2.314

Table 2. Selected bond lengths [Å], angles and torsion angles [°] for **1**.

Au1-S1	2.269(2)	Au2-S4	2.278(3)
Au1-S2	2.278(3)	Au2-S3	2.279(2)
S1-C11	1.721(9)	S3-C31	1.707(9)
S2-C21	1.729(12)	S4-C41	1.688(11)
S1-Au1-S2	172.10(11)	S4-Au2-S3	172.14(10)
C11-S1-Au1	105.3(3)	C31-S3-Au2	106.8(3)
C21-S2-Au1	103.8(3)	C41-S4-Au2	106.8(4)
C11-S1···S2-C21	111.4(5)	Au1-S2-C21-N21	$-27.5(10)$
C31-S3···S4-C41	$-111.1(5)$	Au2-S3-C31-N31	19.6(10)
Au1-S1-C11-N11	$-16.3(9)$	Au2-S4-C41-N41	20.9(11)

Table 3. Selected bond lengths [Å], angles and torsion angles [°] for **2**.

Au1-S1	2.285(2)	Au2-S4	2.292(2)
Au1-S2	2.285(2)	Au2-S3	2.293(2)
S1-C11	1.730(10)	S3-C31	1.710(10)
S2-C21	1.745(8)	S4-C41	1.713(9)
S1-Au1-S2	171.83(9)	S4-Au2-S3	171.54(8)
C11-S1-Au1	106.7(3)	C31-S3-Au2	106.8(3)
C21-S2-Au1	108.0(3)	C41-S4-Au2	105.9(3)
C11-S1···S2-C21	$-71.9(4)$	Au1-S2-C21-N21	9.9(8)
C31-S3···S4-C41	70.3(4)	Au2-S3-C31-N31	$-13.8(8)$
Au1-S1-C11-N11	19.1(8)	Au2-S4-C41-N41	$-16.9(8)$

The packing is further complicated by Au···N contacts in **1** and Au···O and Au···S in **3**.

Experimental Section

Physical measurements

These were recorded as described in [1].

Preparations

The compounds were prepared from the corresponding chloride salts [1] as follows: 1 mmol of the chloride salt was dissolved in 50 ml of ethanol (for **1**) or suspended in 30 ml of methanol (for **2** and **3**), and treated with a solution of silver camphor-10-sulfonate (1 mmol) in acetonitrile (5 ml). The cloudy reaction mixture was stirred for 1.5 h at room temperature with exclusion of light. After filtering off the precipitated AgCl, the colourless filtrate was stored at -18 °C for 12 h, whereupon the products crystallized (**2** as the solvate with $^1/_2$ CH_3CN and $^1/_2$ CH_3OH).

Bis(imidazolidine-2-thione)gold(I) camphor-10-sulfonate (**1**)

Yield: 0.303 g (70%); dec. > 201 °C; ^{1}H NMR (d_6-DMSO): $\delta = 0.74$ [3H, s; C(9)H_3], 1.05 [3H, s; C(8)H_3], 1.27 [2H, m; C(2)H_{ax} + C(3)H_{ax}], 1.80 [1H, t, ^4J(H - H) = 18.2 Hz; C(5)H_2], 1.93 [2H, m; C(3)H_{eq} + C(4)H], 2.24 [1H, dt, ^4J(H - H) = 18.2 Hz, ^3J(H - H) = not separated; C(5)H_{ax}],

Table 4. Selected bond lengths [Å], angles and torsion angles [°] for **3**.

Au1-S2	2.2877(19)	Au2-S3	2.2861(18)
Au1-S1	2.2930(19)	Au2-S4	2.2890(18)
S1-C11	1.717(7)	S3-C31	1.717(7)
S2-C21	1.714(8)	S4-C41	1.720(7)
C11-S11	1.710(7)	C31-S31	1.707(7)
C13-S11	1.825(6)	C33-S31	1.820(7)
C21-S21	1.697(7)	C41-S41	1.704(7)
C23-S21	1.827(8)	C43-S41	1.815(7)
S2-Au1-S1	172.11(7)	S3-Au2-S4	172.23(7)
C11-S1-Au1	105.6(2)	C31-S3-Au2	105.9(2)
C11-S11-C13	92.6(3)	C31-S31-C33	91.9(3)
C21-S2-Au1	104.7(2)	C41-S4-Au2	104.0(2)
C21-S21-C23	92.9(4)	C41-S41-C43	92.8(3)
C11-S1···S2-C21	9.1(4)	Au1-S2-C21-S21	−5.5(5)
C31-S3···S4-C41	−9.8(4)	Au2-S3-C31-S31	15.6(5)
Au1-S1-C11-S11	−0.9(5)	Au2-S4-C41-S41	10.3(5)

Table 5. Hydrogen bonds [Å,°] for compound **1**.

System D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
a: N11-H11···O1	0.89(2)	2.05(2)	2.908(10)	163(6)
b: N21-H21···O2	0.88	2.18	2.977(10)	151
c: N31-H31···O5	0.88	2.05	2.854(10)	151
d: N41-H41···O6	0.93(2)	2.05(2)	2.926(11)	158(5)
e: N22-H22···O7	0.90(2)	1.91(4)	2.766(11)	158(10)
f: N42-H42···O3	0.88(2)	1.97(2)	2.834(11)	169(8)
g: N12-H12···O2#1	0.88(2)	1.90(2)	2.774(10)	174(8)
h: N32-H32···O6#2	0.88(2)	1.96(2)	2.833(10)	176(8)
C12-H12A···O4#3	1.08	2.31	3.372(12)	167
C32-H32B···O8#4	1.08	2.56	3.550(14)	152
C105-H10F···O8#5	1.08	2.36	3.334(12)	149
C205-H20E···O4#6	1.08	2.56	3.505(15)	145
C110-H11A···S1#7	1.08	2.94	3.792(9)	136
C210-H21B···S3#8	1.08	2.79	3.835(10)	163
C13-H13B···Au1#1	1.08	3.07	3.969(10)	142
C204-H204···Au1#9	1.08	3.09	3.910(10)	133

Symmetry transformations used to generate equivalent atoms: #1 $-x,y+1/2,-z+1$; #2 $-x+1,y-1/2,-z$; #3 $x,y+1,z$; #4 $x,y-1,z$; #5 $x,y-1,z+1$; #6 $x,y+1,z-1$; #7 $-x,y-1/2,-z+1$; #8 $-x+1,y+1/2,-z$; #9 $-x,y+1/2,-z$.

2.38 [1H, d, ^4J(H - H) = 14.7 Hz; C(10)H_2], 2.69 [1H, m; C(2)H_{eq}], 2.88 [1H, d, ^4J(H - H) = 14.7 Hz; C(10)H_2], 3.36 [4H, s; etu-CH_2], 3.76 [4H, s; etu-CH_2], 9.33 [4H, bs; NH]; MS (NBA): FAB (neg.) *m/z* = 229 (2%, [A - 2H]$^-$), 231 (100%, [A]$^-$), 233 (8%, [A + 2H]$^-$); FAB (pos.) = 103 (4%, [K - Au($C_3H_6N_2S$) + H]$^+$), 299 (22%, [K - ($C_3H_4N_2S$)]$^+$), 401 (100%, [K]$^+$), 699 (4%, [2K - ($C_3H_6N_2S$) – H]$^+$). Elemental analysis for $C_{16}H_{27}AuN_4O_4S_3$ (632.62): calcd. C 30.38, H 4.31, N 8.86, S 15.20; found C 30.02, H 4.26, N 8.82, S 15.13.

Bis(1-methyl-imidazolidine-2-thione)gold(I) camphor-10-sulfonate (**2**)

Yield: 0.102 g (31%); m.p.: 192 °C; ^{1}H-NMR (d_6-DMSO): $\delta = 0.75$ [3H, s; C(9)H_3], 1.05 [3H, s; C(8)H_3],

Table 6. Hydrogen bonds [Å,°] for compound **2**.

System D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
a: N(11)-H(11)···O(1)	0.79(3)	1.99(3)	2.781(10)	175(7)
b: N(21)-H(21)···O(1)	0.79(3)	2.10(4)	2.838(9)	157(7)
c: N(31)-H(31)···O(7)	0.79(3)	2.03(3)	2.823(10)	176(7)
d: N(41)-H(41)···O(7)	0.77(3)	2.13(5)	2.820(10)	149(8)
e: N(21)-H(21)···O(4)	0.79(3)	2.68(3)	3.136(9)	119(3)
C(33)-H(33A)···O(4)#2	1.08	2.34	3.268(10)	143
O(98)-H(98)···N(99)	0.84	2.16	2.980(15)	165
C(98)-H(98A)···O(6)	1.08	2.40	3.407(10)	155
C(205)-H(20H)···O(5)#1	1.08	2.36	3.397(11)	160
C(105)-H(10E)···O(2)#1	1.08	2.44	3.424(8)	151
C(98)-H(98C)···O(2)#3	1.08	2.59	3.402(10)	132
C(209)-H(20A)···O(98)#1	1.08	2.60	3.549(13)	163
C(34)-H(34B)···Au(1)#2	1.08	3.16	4.194(9)	161
C(34)-H(34B)···S(2)#2	1.08	3.02	4.009(10)	153
C(24)-H(24B)···Au(2)#3	1.08	3.20	4.195(9)	153

Symmetry transformations used to generate equivalent atoms: #1 $x+1,y,z$; #2 $-x+1,y-1/2,-z+1$; #3 $-x,y+1/2,-z+1$.

Table 7. Hydrogen bonds [Å,°] for compound **3**.

System D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
f: N(11)-H(11)···O(7)#1	0.79(4)	1.95(4)	2.715(7)	163(5)
a: N(21)-H(21)···O(1)	0.78(4)	2.19(4)	2.919(9)	154(5)
b: N(21)-H(21)···O(3)	0.78(4)	2.57(6)	3.071(9)	124(6)
c: N(31)-H(31)···O(3)	0.79(4)	1.98(4)	2.741(8)	163(6)
d: N(41)-H(41)···O(5)	0.80(4)	2.30(5)	2.929(9)	137(7)
e: N(41)-H(41)···O(6)	0.80(4)	2.33(4)	3.093(9)	160(5)
C(12)-H(12B)···O(2)#3	1.08	2.34	3.168(9)	132
C(13)-H(13B)···O(2)#3	1.08	2.46	3.239(8)	128
C(22)-H(22B)···O(5)#2	1.08	2.50	3.242(10)	125
C(23)-H(23B)···O(5)#2	1.08	2.24	3.109(10)	136
C(32)-H(32A)···O(7)#2	1.08	2.40	3.147(9)	125
C(33)-H(33A)···O(7)#2	1.08	2.56	3.294(8)	124
C(32)-H(32B)···O(6)#3	1.08	2.57	3.369(10)	130
C(33)-H(33B)···O(8)#4	1.08	2.32	3.203(9)	138
C(43)-H(43A)···O(1)#5	1.08	2.35	3.302(8)	146
C(13)-H(13A)···O(4)#2	1.08	2.45	3.186(8)	124
C(205)-H(20F)···S(1)#6	1.08	2.80	3.838(7)	161
C(105)-H(10F)···S(3)#7	1.08	2.79	3.843(8)	166
C(23)-H(23A)···S(4)#3	1.08	2.82	3.815(9)	154
C(43)-H(43B)···S(2)#8	1.08	2.92	3.803(8)	139
C(205)-H(20E)···S(2)#7	1.08	2.93	3.835(8)	141
C(205)-H(20E)···S(41)#9	1.08	2.93	3.722(7)	130

Symmetry transformations used to generate equivalent atoms: #1 $x,y,z-1$; #2 $-x+1 1/2,-y+1,z-1/2$; #3 $-x+1/2,-y+1,z-1/2$; #4 $-x+1,y-1/2,-z+1/2$; #5 $-x+1/2,-y+1,z+1/2$; #6 $x-1/2,-y+1 1/2,-z$; #7 $x+1/2,-y+1 1/2,-z$; #8 $-x+1 1/2,-y+1,z+1/2$; #9 $-x+1,y+1/2,-z+1/2$.

1.28 [2H, m; C(2)H_{ax} + C(3)H_{ax}], 1.80 [1H, d, ^4J(H - H) = 1801 Hz; C(5)H_{eq}], 1.84 [1H, m; C(3)H_{eq}], 1.94 [1H, t, ^3J(H - H) = 4.3 Hz; C(4)H], 2.20 [1H, m; C(5)H_{ax}], 2.37 [1H, d, ^4J(H – H) = 14.7 Hz; C(10)H_2], 2.67 [1H, m; C(2)H_{eq}], 2.88 [1H, d, ^4J(H - H) = 14.7 Hz; C(10)H_2], 3.07 [6H, s, NCH_3], 3.64 [4H, m, 2nd order spectrum of *ABNM* spin system; CH_2], 3.87 [4H, m, 2nd order spectrum of *ABNM* spin system; CH_2], 9.15 [2H, bs; NH]. MS (NBA): FAB (neg.) *m/z* = 231 (100%, [A]$^-$), 232 (12%, [A + 1H]$^-$), 233 (7%, [A

+ 2H]$^-$); FAB (pos.) *m/z* = 136 (34%, [A - O_3SCH_2 - H]$^+$), 313 (18%, [K - (CH_3-$C_3H_6N_2S$)]$^+$), 399 (4%, [K - $2CH_3$]$^+$), 427 (12%, [K - 2H]$^+$), 429 (100%, [K]$^+$), 430 (13%, [K + H]$^+$), 741 (4%, [2K - (CH_3-$C_3H_6N_2S$)]$^+$). Elemental analysis for $C_{16}H_{31}AuN_4O_4S_3$ (660.68): calcd. C 32.72, H 4.74, N 8.48, S 14.56; found C 32.38, H 4.65, N 8.33, S 14.55.

Bis(1,3-thiazolidine-2-thione)gold(I) camphor-10-sulfonate (**3**)

Yield: 0.341 g (51%); dec. > 164 °C; ^{1}H NMR (d_6-DMSO): $\delta = 0.74$ [3H, s; C(9)H_3]; 1.04 [3H, s; C(8)H_3], 1.29 [2H, m; C(2)H_{ax} + C(3)H_{ax}], 1.79 [1H, d, ^4J(H - H) = 18.2 Hz; C(5)H_{eq}], 1.84 [1H, m; C(3)H_{eq}] 1.94 [1H, t, ^3J(H - H) = 4.4 Hz; C(4)H], 2.24 [1H, dt, ^4J(H - H) = 18.2 Hz, ^3J(H - H) = not seperated; C(5)H_{ax}], 2.39 [1H, d, ^4J(H - H) = 14.7 Hz; CH_2], 2.67 [1H, m; C(2)H_{eq}], 2.88 [1H, d, ^4J(H - H) = 14.7 Hz; CH_2], 3.68 [4H, t, ^3J(H - H) = 8.4 Hz; CH_2], 4.23 [4H, t, ^3J(H - H) = 8.4 Hz; CH_2]; 11.8 [2H, bs, NH]; MS (NBA): FAB (neg.) *m/z* = 231 (100%, [A]$^-$), 233 (6%, [A + 2H]$^-$); FAB (pos.) *m/z* = 136 (34%, [A - O_3SCH_2 - H]$^+$), 316 (26%, [K - ($C_3H_6NS_2$)]$^+$), 435 (100%, [K]$^+$), 437 (17%, [K + 2H]$^+$), 630 (6%, [K + Au - 2H]$^+$), 631 (24%, [K + Au - H]$^+$), 748 (6%, [2K - ($C_3H_6NS_2$) - 3H]$^+$), 750 (24%, [2K - ($C_3H_6NS_2$) - H]$^+$), 752 (18%, [2K - ($C_3H_6NS_2$) + H]$^+$); Elemental analysis for $C_{16}H_{25}AuN_4O_4S_3$ (666.70): calcd. C 28.82, H 3.79, N 4.20, S 24.04; found C 27.96, H 3.72, N 4.30, S 24.28.

X-ray structure determinations: The crystals were mounted in inert oil on glass fibres. Data were measured using Mo-K_α radiation ($\lambda = 0.71073$ Å) on *Siemens* (**3**) or *Bruker* SMART 1000 CCD diffractometers (**1**, **2**), fitted with low temperature attachments. Structures were solved by direct methods and refined anisotropically on F^2 [6]. The pseudosymmetry in the structure of **1** (see Discussion) caused problems with double images during the refinement. Crystal data and refinement details are presented in Table 1; selected molecular dimensions in Tables 2 – 4; and hydrogen bond dimensions in Tables 5 – 7. *General hydrogen atom treatment*: Hydrogen atoms bonded to nitrogen atoms were located in Fourier syntheses and refined freely, but with N-H and C(-N-)H distances restrained to be equal using the *SADI* instruction where possible [6]; these H atoms cannot be geometrically positioned with certainty because their parent nitrogen atoms do not in general have a planar substituent geometry. Methyl hydrogens were located in difference syntheses, idealised and refined as rigid groups allowed to rotate but not tip. Other hydrogen atoms were placed in calculated positions and refined using a riding model. *Exceptions to the above*: (**1**), H21 and H31 could not be refined stably and were therefore fixed; (**2**), methyl hydrogens at C108 and C97 (methanol) were poorly resolved; the methanol OH hydrogen was geometrically positioned to be consistent with a hydrogen bond to the neighbouring acetonitrile (see Discussion).

For the calculation of hydrogen bonding parameters, C-H bond lengths were normalised to 1.08 Å. Contacts with angles < 130° at hydrogen have generally been omitted, unless forming part of three-centre or bifurcated systems.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-224851 (**1**), 224852 (**2**) and 224853 (**3**). Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (E-mail: deposit@ccdc.cam.ac.uk).

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