Secondary Interactions in Gold(I) Complexes with Thione Ligands, 3. Three Ionic Dimesylamides [1, 2]

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Three structures of the form bis(thione)gold(I) di(methanesulfonyl)amide [thione = imidazolidine-2-thione, **1**; 1-methyl-imidazolidine-2-thione, **2**; thiazolidine-2-thione, **3**] were determined; all crystallize with one formula unit in the asymmetric unit. Each N-H hydrogen bond donor forms one classical two-centre hydrogen bond with an anion acceptor. Compound **1** thereby forms a complex layer structure with a layer thickness of 10.17 Å; the packing may be analysed in terms of thinner subunit layers consisting of interlinked, hydrogen-bonded chains and rings. Compound **2** forms a chain structure consisting of a series of "hairpin bends", a common feature in the gold complexes of 1-alkyl-imidazolidine-2-thiones. Compound **3** forms a corrugated ribbon structure in which the central region consists of parallel S-Au-S axes linked by aurophilic interactions; the anions exercise a "clamping" function by forming hydrogen bonds at the periphery of the ribbons. Further short contacts can be classed as weak hydrogen bonds C-H···X, with X = N, O, S or Au.

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

Introduction

Our previous studies of secondary interactions in gold(I) complexes of heterocyclic ligands bearing a thione group have involved chloride [3] and camphorsulfonate salts [1] of the complex cations $[L_2Au]^+$ with L = imidazolidine-2-thione ("ethylenethiourea", etu), 1-methyl-imidazolidine-2-thione (Me-etu) and thiazolidine-2-thione (tzt). As would be expected, the crystal packing patterns were completely different for the small, spherical chloride ion from those of the large, enantiomerically pure camphorsulfonate; the earlier publications may be consulted for further introductory material. Here we have used di(methanesulfonyl)amide ("dimesylamide", DMS), $[N(SO_2CH_3)_2]^-$, as the counteranion; it is qualitatively different from the previously used anions in that it possesses five classical hydrogen bond acceptors, and, despite its apparent flexibility, it almost always presents the same conformation in the solid state (see below). We have again determined the three structures of the series $[L_2Au]^+DMS^-$ with L = etu (**1**), Me-etu (**2**) and tzt (**3**).

Discussion

General aspects

All three compounds crystallize solvent-free in centrosymmetric space groups with one formula unit in the asymmetric unit (Figs 1 – 3). The DMS anions display their usual solid-state conformation [4], with approximate twofold symmetry along the bisector of the S-N-S angle, two antiperiplanar (*ap*; O1, O3) and two synclinal oxygen atoms (*sc*; O2, O4); the extremely close approximation to twofold symmetry in the current structures may be judged from $\Delta\tau_{SN}$, the mean difference in symmetry-related absolute torsion angles, which is 2.1° for **1**, 0.8° for **2** and 0.3° for **3**.

All complexes display bond lengths and angles broadly as expected, *e. g.* S−Au−S bond angles close to linearity, with values of 176 – 178°, Au-S bond lengths, which lie in the narrow range 2.286 – 2.299 Å, or the angles at sulfur, 102 – 105°. For individual values, Tables 2 – 4 or the Supplementary Material may be consulted.

Our previous publications [1, 3] established that the most relevant structural degree of freedom in

Compound	1	2	3
Formula	$C_8H_{18}AuN_5O_4S_4$	$C_{10}H_{22}AuN_5O_4S_4$	$C_{16}H_{25}AuN_2O_4S_5$
M_r [g/mol]	573.48	601.53	666.65
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Cell dimensions [Å, °]	$a = 8.6188(8)$	$a = 9.1268(8)$	$a = 5.5716(10)$
	$b = 10.0429(10)$	$b = 9.2452(8)$	$b = 13.664(2)$
	$c = 11.4471(14)$	$c = 12.5291(10)$	$c = 23.212(4)$
	$\alpha = 65.098(8)$	$\alpha = 95.224(6)$	$\alpha = 90$
	$\beta = 73.503(8)$	$\beta = 100.672(6)$	$\beta = 94.473(4)$
	$\gamma = 75.364(8)$	$\gamma = 111.172(6)$	$\gamma = 90$
V [Å³]	851.57(16)	954.29(14)	1761.8(5)
Z	2	2	4
Crystal habit	pale yellow tablet	colourless prism	colourless needle
Crystal size [mm³]	$0.36 \times 0.24 \times 0.12$	$0.20 \times 0.18 \times 0.14$	$0.22 \times 0.03 \times 0.02$
D_x [g/cm³]	2.237	2.093	2.291
$2\theta_{max}$ [°]	55	50	57
μ [mm⁻¹]	9.15	8.17	9.08
Temperature [K]	173	173	143
Absorption correction	psi-scans	psi-scans	multiple scans (SADABS)
T_{min} / T_{max}	0.96 / 0.38	0.89 / 0.66	0.99 / 0.70
Measured reflections	4531	7606	13172
Independent reflections	3773	3343	4493
R_{int}	0.014	0.017	0.072
$F(000)$	552	584	1168
Restraints	26	1	11
Parameters	217	230	209
S	0.95	0.88	0.76
$R1[F^2 > 2\sigma(F^2)]$	0.027	0.015	0.034
$wR2(F^2$, all refl.)	0.063	0.032	0.051
$\Delta\rho_{min}$ / $\Delta\rho_{max}$ [eÅ⁻³]	1.8 / −1.6	0.48 / −0.45	1.52 / −1.10

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

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

Au-S(1)	2.2976(12)	S(1)-C(11)	1.721(5)
Au-S(2)	2.2985(13)	S(2)-C(21)	1.720(4)
S(1)-Au-S(2)	175.95(5)	C(21)-S(2)-Au	104.87(16)
C(11)-S(1)-Au	105.43(16)	S(4)-N(1)-S(3)	120.1(2)
C11-S1···S2-C21	−174.0(2)	S(4)-N(1)-S(3)-C(1)	−79.3(3)
Au-S(1)-C(11)-N(11)	16.9(4)	S(3)-N(1)-S(4)-O(3)	167.4(3)
Au-S(2)-C(21)-N(21)	6.3(5)	S(3)-N(1)-S(4)-O(4)	41.9(3)
S(4)-N(1)-S(3)-O(2)	38.6(4)	S(3)-N(1)-S(4)-C(2)	−76.7(3)
S(4)-N(1)-S(3)-O(1)	167.0(3)		

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

Au-S(1)	2.2856(10)	S(1)-C(11)	1.722(4)
Au-S(2)	2.2904(10)	S(2)-C(21)	1.720(4)
S(1)-Au-S(2)	178.34(4)	C(21)-S(2)-Au	103.87(13)
C(11)-S(1)-Au	104.91(13)	S(4)-N(1)-S(3)	121.09(16)
C11-S1···S2-C21	−167.52(13)	S(4)-N(1)-S(3)-C(1)	85.2(2)
Au-S(1)-C(11)-N(11)	5.5(3)	S(3)-N(1)-S(4)-O(4)	−33.7(3)
Au-S(2)-C(21)-N(21)	−0.6(3)	S(3)-N(1)-S(4)-O(3)	-162.59(19)
S(4)-N(1)-S(3)-O(2)	−33.0(3)	S(3)-N(1)-S(4)-C(2)	85.1(2)
S(4)-N(1)-S(3)-O(1)	−161.02(19)		

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

Au-S(1)	2.2927(15)	C(11)-S(11)	1.715(5)
Au-S(2)	2.2962(15)	C(13)-S(11)	1.822(6)
Au-Au#1	3.4045(7)	S(2)-C(21)	1.702(6)
Au-Au#2	3.4305(7)	C(21)-S(21)	1.725(6)
S(1)-C(11)	1.714(6)	C(23)-S(21)	1.808(6)
S(1)-Au-S(2)	176.21(6)	C(11)-S(1)-Au	102.48(19)
S(1)-Au-Au#1	84.47(4)	C(11)-S(11)-C(13)	91.5(3)
S(2)-Au-Au#1	99.24(4)	C(21)-S(2)-Au	101.99(19)
S(1)-Au-Au#2	89.46(4)	C(21)-S(21)-C(23)	91.4(3)
S(2)-Au-Au#2	90.05(4)	S(4)-N(1)-S(3)	121.9(3)
Au#1-Au-Au#2	109.20(2)		
C11-S1···S2-C21	90.0(3)	S(4)-N(1)-S(3)-C(1)	76.7(4)
Au-S(1)-C(11)-S(11)	9.1(4)	S(3)-N(1)-S(4)-O(3)	−169.6(3)
Au-S(2)-C(21)-S(21)	−40.2(4)	S(3)-N(1)-S(4)-O(4)	−41.7(4)
S(4)-N(1)-S(3)-O(2)	−41.6(4)	S(3)-N(1)-S(4)-C(2)	76.4(4)
S(4)-N(1)-S(3)-O(1)	−169.0(3)		

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

the cations is the torsion angle C-S···S-C. The complex cations in 1 and 2 show similar antiperipla-

nar conformations [torsion angles $−174.0(2)°$ (1) and $−167.5(1)°$ (2)], whereas the corresponding value in 3 is $90.0(3)°$ (Figs 1–3). As we have previously noted [3], the extreme flexibility of the cations makes effective planning of the crystal packing ("crystal engineer-

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

System: D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	∠(DHA)
a: N(11)-H(11)⋯O(1)	0.88(3)	1.99(4)	2.799(6)	153(5)
b: N(12)-H(12)⋯N(1)#1	0.87(3)	2.08(4)	2.926(5)	165(5)
c: N(21)-H(21)⋯O(3)#2	0.88(3)	1.96(4)	2.820(5)	165(5)
d: N(22)-H(22)⋯O(4)#3	0.88(3)	1.96(4)	2.831(5)	171(6)
e: C(2)-H(2A)⋯O(4)#4	1.08	2.38	3.437(6)	163
f: C(2)-H(2C)⋯O(2)#5	1.08	2.50	3.468(6)	149
g: C(1)-H(1B)⋯S(2)	1.08	2.80	3.674(6)	138
h: C(22)-H(22B)⋯S(2)#6	1.08	2.81	3.779(5)	150
i: C(22)-H(22B)⋯Au#6	1.08	3.07	3.845(5)	129
j: C(23)-H(23A)⋯Au#6	1.08	2.95	3.748(5)	131
k: C(22)-H(22A)⋯S(1)#7	1.08	2.92	3.900(5)	151
l: C(1)-H(1C)⋯N(11)#8	1.08	2.58	3.531(7)	146

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

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(3)	0.81(3)	2.08(3)	2.832(4)	155(4)
b: N(21)-H(21)⋯O(1)#1	0.83(3)	2.20(3)	2.895(4)	142(3)
c: C(13)-H(13B)⋯O(2)#2	1.08	2.50	3.337(4)	133
d: C(13)-H(13B)⋯O(4)#2	1.08	2.67	3.586(4)	154
e: C(1)-H(1B)⋯O(1)#3	1.08	2.46	3.493(4)	161
f: C(12)-H(12A)⋯O(2)#2	1.08	2.60	3.388(4)	129
g: C(12)-H(12B)⋯O(2)#4	1.08	2.54	3.356(4)	132
h: C(14)-H(14B)⋯O(4)#2	1.08	2.57	3.548(4)	150
i: C(23)-H(23A)⋯N(1)#5	1.08	2.44	3.382(4)	145
j: C(22)-H(22B)⋯O(3)#5	1.08	2.66	3.414(4)	126
k: C(23)-H(23B)⋯O(3)#7	1.08	2.67	3.470(4)	131
l: C(13)-H(13A)⋯Au#6	1.08	2.91	3.781(3)	138
m: C(14)-H(14C)⋯Au#6	1.08	2.83	3.739(4)	142
n: C(23)-H(23B)⋯Au#7	1.08	2.85	3.773(3)	143
o: C(24)-H(24A)⋯Au#7	1.08	3.19	4.036(4)	136

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

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

System: D-H⋯A	d(D-H)	d(H⋯A)	d(D⋯A)	∠(DHA)
a: N(21)-H(21)⋯O(1)	1.09(5)	1.73(5)	2.787(6)	164(6)
b: N(11)-H(11)⋯N(1)#2	1.08(5)	1.76(5)	2.813(7)	164(5)
c: C(1)-H(1A)⋯O(1)#6	1.08	2.54	3.538(7)	153
d: C(2)-H(2B)⋯O(4)#7	1.08	2.26	3.325(7)	170
e: C(12)-H(12B)⋯O(4)#1	1.08	2.57	3.571(7)	155
f: C(13)-H(13A)⋯O(4)#3	1.08	2.42	3.397(7)	151
g: C(13)-H(13B)⋯S(1)#4	1.08	2.79	3.722(6)	144
h: C(22)-H(22B)⋯O(2)#5	1.08	2.48	3.477(7)	152

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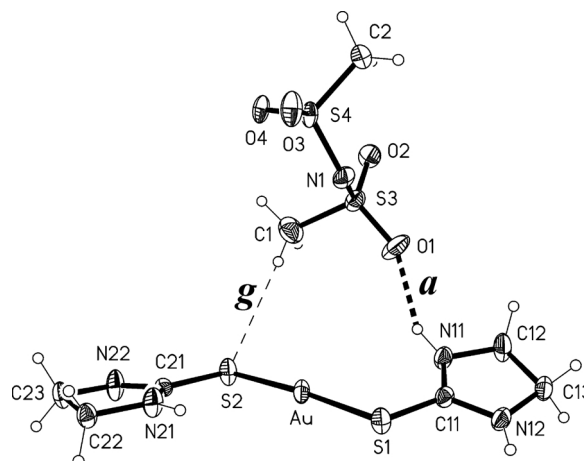

Fig. 1. Bis(imidazolidine-2-thione)gold(I) dimesylamide, **1**, asymmetric unit with numbering scheme. Thermal ellipsoids are shown with 50% probability. Hydrogen radii are arbitrary. Dashed lines represent classical hydrogen bonds (thick) and non-classical hydrogen bonds (thin), labelled with italic letters, corresponding to Table 5.
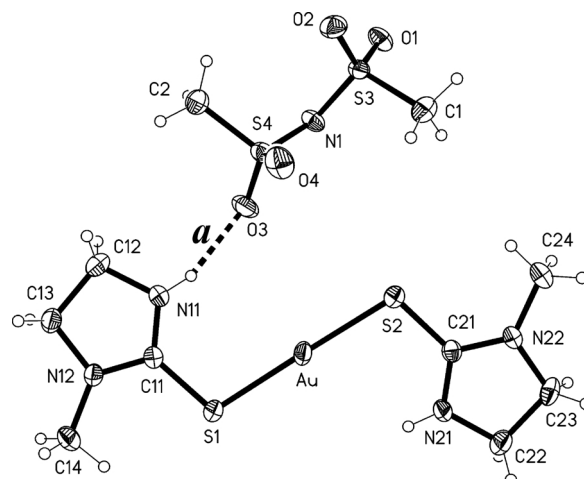

Fig. 2. Bis(1-methyl-imidazolidine-2-thione)gold(I) dimesylamide, **2**, asymmetric unit with numbering scheme. Thermal ellipsoids are shown with 50% probability. Hydrogen radii are arbitrary. The dashed line represents a hydrogen bond, labelled with italic letters, corresponding to Table 6.

ing") at best a difficult exercise. A further conformational degree of freedom, for the asymmetric thiourea ligands tzt and Me-etu, is the *endo* or *exo* direction of the NH groups. In the heterocyclic rings of com-

pound **2**, the NH groups are *endo* (nearer the gold centres) (Fig. 2), while the N-Me groups point outwards; in compound **3**, the ring sulfurs are *endo* and the NH groups *exo* (Fig. 3).

For compounds **1** and **2**, 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
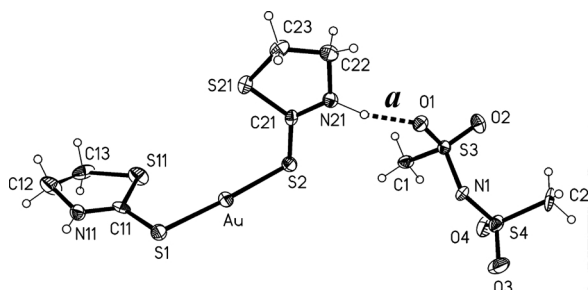
Fig. 3. Bis(1,3-thiazolidine-2-thione)gold(I) dimesylamide, **3**, asymmetric unit with numbering scheme. Thermal ellipsoids are shown with 50% probability. Hydrogen radii are arbitrary. The dashed line represents a hydrogen bond, labelled with italic letters, corresponding to Table 7.

angles are $12°$ and $3°$, respectively), as was previously observed [1, 3], but the second ring of compound **3** is less planar (mean deviation 0.14 Å) and the torsion angle Au-S2-C21-S21 is $-40.2(4)°$, a further departure from the previously established structural principles.

Many gold(I) species display short "aurophilic contacts" [5] between formally non-bonded gold atoms, but these are not a common feature of the thione complexes; such contacts are absent in compound **1**, with

a shortest Au···Au distance of 6.96 Å, and in **2**, with a corresponding distance of 7.02 Å (for compound **3**, see below).

Crystal packing: classical hydrogen bonds

Compound **1** has four classical hydrogen bond donors (the four NH groups) and five acceptors (the anion N and four O atoms). Four two-centre hydrogen bonds are formed, whereby the potential acceptor O2 is not involved. The initial impression is of a three-dimensional packing system (Fig. 4), but in fact the structure consists of layers that are one cell thick and parallel to (100) (perpendicular distance between faces: 10.17 Å). These layers may be analysed in terms of a relatively simple subunit, also a layer but much thinner and parallel to $(10\bar{1})$ (Fig. 5). The atom sequence H21···O3-S4-O4···H22 leads to chains parallel to the y axis, which can be described on the secondary level by the graph set $N_2(c,d) = C_2^2(8)$. The sequence H12···N1-S3-O1···H11, in contrast, forms inversion-symmetric rings, following the graph set $R_4^4[N_2(a,b)]$. The layer also contains short contacts Au···O3, 3.363(3) Å.

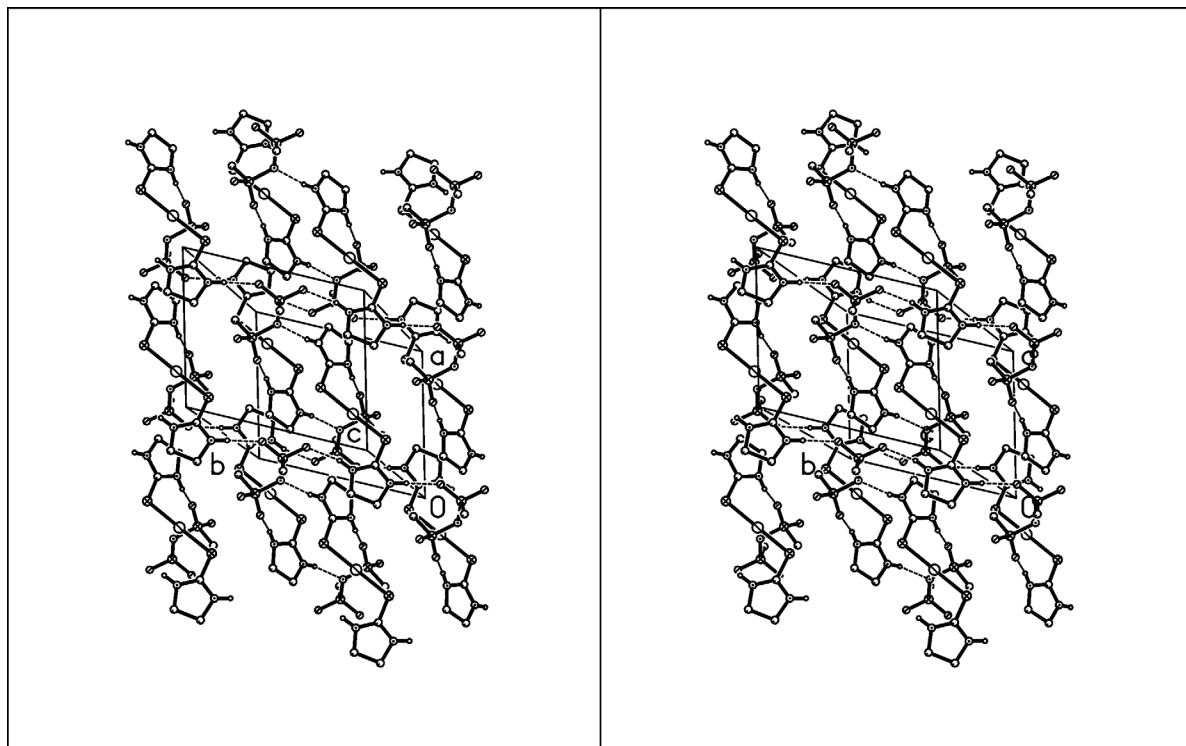
Fig. 4. Compound **1**, stereo view of the complete layer structure viewed perpendicular to the *xy* plane (the thickness of the layer, *ca.* 10 Å, makes a mono view difficult to interpret). Dashed lines represent classical hydrogen bonds.
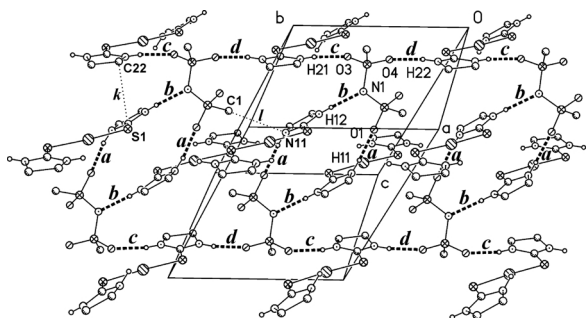
Fig. 5. Compound **1**, thinner section of the layer structure viewed perpendicular to $(10\bar{1})$. Dashed lines represent classical hydrogen bonds. Thick (thin) dashed lines represent classical (non-classical) hydrogen bonds, labelled with italic letters, corresponding to Table 5; for clarity, only one of each type of non-classical hydrogen bond *k* and *l* is shown, in the top left-hand corner. Au···O interactions are not shown.
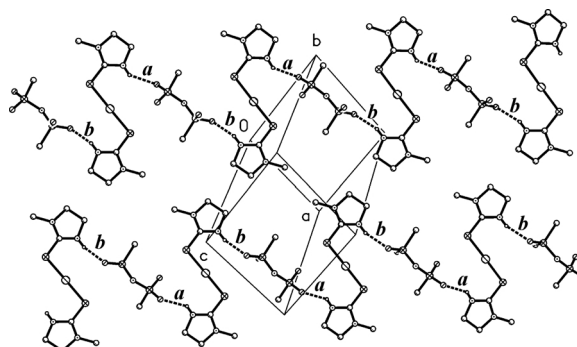

Fig. 6. Compound **2**, chain structure viewed perpendicular to $(\bar{1}\,12)$. Dashed lines represent classical hydrogen bonds, labelled with italic letters, corresponding to Table 6.

Compound **2**, with its two donor NH functions, forms two two-centre hydrogen bonds, one each to the *ap* oxygens O1 (by translation $1+x, 1+y, z$) and O3 (Fig. 6). The net effect is to link the cations and anions to form a chain with overall direction parallel to [110]; the chain consists of a series of "hairpin bends" with the binary graph set $N_2(a,b) = C_2^2(14)$.

The same topological sequence, but with chloride instead of DMS, was observed for $[(R\text{-etu})_2\text{Au}]^+\text{Cl}^-$ (R = Me [3], ^{i}Pr [6]), and may be considered as a robust packing motif, for which an antiperiplanar C-S···S-C conformation is a precondition. However, the corresponding camphorsulfonate salt does not display this pattern [1].

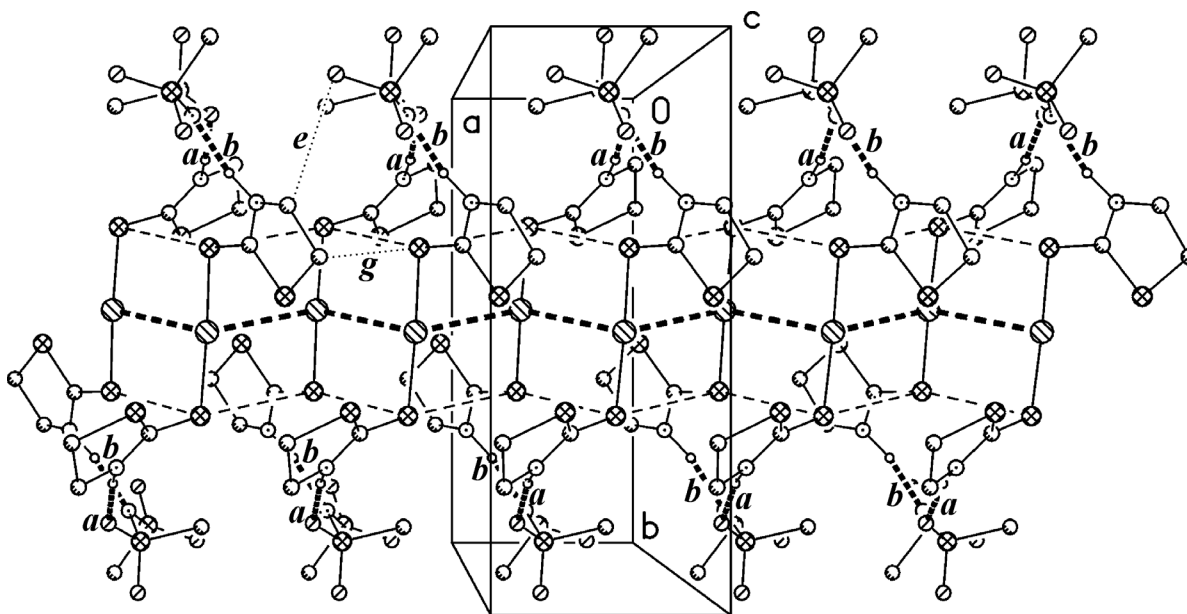Compound **3** also has two donor NH functions and forms two two-centre hydrogen bonds, but now to the

Fig. 7. Compound **3**, ribbon structure viewed perpendicular to the *xy* plane. Thick (thin) dashed lines represent classical (non-classical) hydrogen bonds, labelled with italic letters, corresponding to Table 7; for clarity, only one of each type of non-classical hydrogen bond *e* (O4···C12) and *g* (C13···S1) is shown, in the top left-hand corner. Aurophilic interactions and S···S contacts are displayed as unlabelled thick and thin dashed lines, respectively. Contacts Au···S and S11···S21 are omitted for clarity. Values not given elsewhere in text: Au···S11 4.034(2), 4.073(2); Au···S1 3.917(2), 4.108(2); S1···S2 3.415(2), 3.553(2); S11···S21 3.470(2) Å.
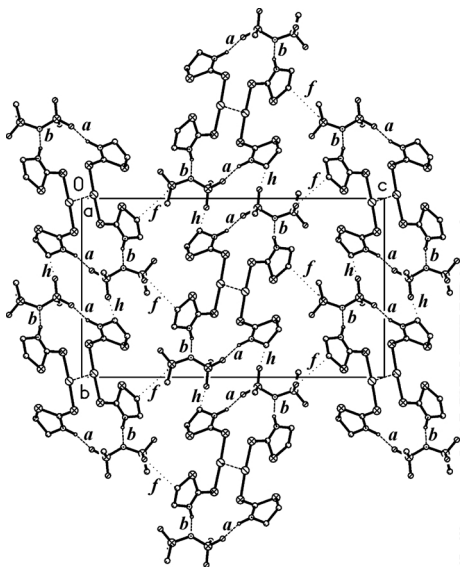
Fig. 8. Compound **3**, projection parallel to the *x* axis. Thick (thin) dashed lines represent the classical (non-classical) hydrogen bonds, labelled with italic letters, corresponding to Table 7, and Au···Au contacts (not labelled).

ap oxygen O1 and the central nitrogen N1 of the anion. On the binary level, these interactions connect the ion pair of the independent unit with an equivalent ion pair to give inversion-symmetric rings parallel to the *yz* plane, with the graph set $N_2(a,b) = R_4^4(24)$ (Figs 7, 8). However, these contacts are peripheral to the main packing feature, which is a zigzag ribbon of parallel S-Au-S moieties linked by aurophilic contacts of 3.4045(7) and 3.4305(7) Å. The zigzag angle Au···Au···Au is 109.20(2)°, with neighbouring gold atoms related *via* the inversion centres at $0, 1/2, 1/2$ and $1/2, 1/2, 1/2$; the overall ribbon direction is parallel to the *x* axis (Fig. 7). Within the ribbon, several Au···S and S···S contacts (*ca.* 4.0 and 3.5 Å respectively) are also observed, and involve both ring and thione sulfurs. The projection parallel to the ribbon direction, given in Fig. 8, shows how the anions are peripheral to the cation chain. A similar association, but forming only dimers, was observed for the camphorsulfonate salts of [(Me-etu)₂Au]⁺ [1].

Crystal packing: anion substructures

An unexpected feature of structures involving the DMS anion is that the anions can associate *via* C-H···O interactions [7]. In compound **1** the anion substructure is formed by ribbons parallel to the *x* axis, consisting of alternating inversion symmetric rings
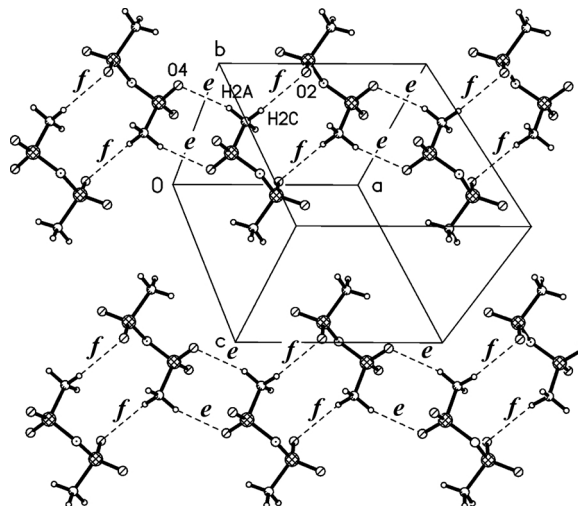

Fig. 9. Compound **1**, anion substructure viewed perpendicular to (011). Dashed lines represent non-classical hydrogen bonds, labelled with italic letters, corresponding to Table 5.

of the complex graph set $N_2(e,f) = R_2^2(8)R_2^2(12)$ (Fig. 9). Compound **2**, in contrast, merely involves centrosymmetric dimers; and compound **3** forms a "ladder" motif of inversion-symmetric $N_1(c) = R_2^2(8)$ rings, connected by the hydrogen bond *d*: C(2)-H(2B)···O(4) to give a double chain that runs parallel to the *x*-axis (Fig. 10), and that can be fully de-
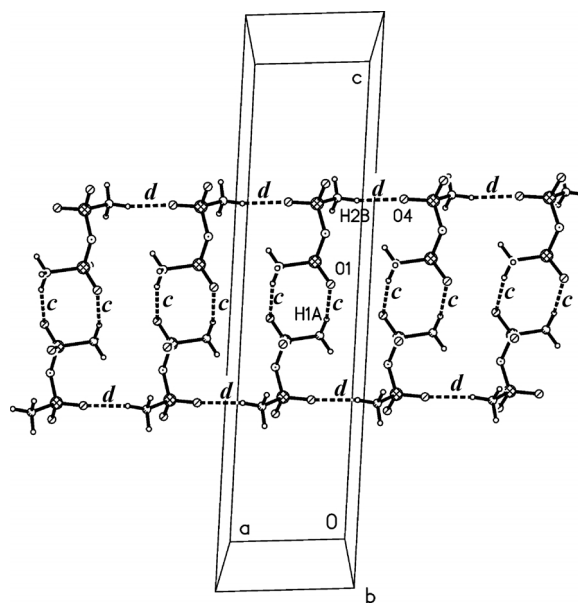

Fig. 10. Compound **3**, anion substructure viewed parallel to the *y* axis. Dashed lines represent non-classical hydrogen bonds, labelled with italic letters, corresponding to Table 7.
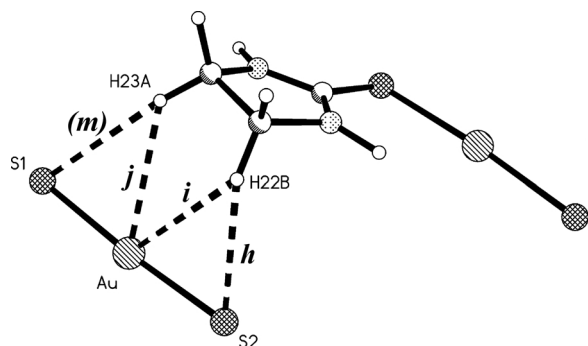
Fig. 11. Compound **1**, close approach of two cations from neighbouring layers. The contact *m:* H23A···S1 (3.08 Å, 167°) is too long to be given in Table 5, but is included here for completeness.

scribed by a graph set of connected $N_2(c,d) = R_4^4(24)$ rings.

Crystal packing: further contacts

Particularly in structures with a surfeit of hydrogen bond acceptors, one may expect "weak" hydrogen bonds of the form C-H···X, where X is a "classical" acceptor (O or N). However, weaker acceptors (S or Au) may also be involved; the combination of weak donor C-H and weak acceptor leads to contacts that may be regarded as borderline hydrogen bonds. Some contacts of the form C-H···O have been outlined in the previous paragraph.

For compound **1**, the asymmetric unit itself displays a short contact H1B···S2 (Fig. 1). The contacts H22A···S1 and H1C···N11 support the sublayer

system (Fig. 5). More striking are a series of contacts C-H···S and C-H···Au between adjacent layers, in which a CH-CH moiety approaches an exposed S-Au-S axis (Fig. 11). However, there is no indication whether these are genuine weak hydrogen bonds or simply a result of the favourable geometry offered by an accessible, linearly coordinated gold centre.

In compound **2**, each cation makes a series of C-H···O contacts to adjacent anions (including a three-centre system from H13B), whereby the *sc* oxygens O2 and O4, which are not involved in classical hydrogen bonds, are the main acceptors. There are also two sets of (C-H)₂···Au contacts to adjacent cations (Fig. 12). The latter are quite short (the shortest is only 2.83 Å), and their non-linearity is explained by the bifurcated acceptor behaviour. There are no C-H···S contacts < Å.

The chain structure of **3**, bracketed at its periphery by the DMS anions and combined with the anion substructure, does not leave much scope for further interactions (Fig. 10). Within the chains, the contacts H12B···O4 and H13B···S1 may provide additional stabilisation, whereas adjacent chains are linked by H13A···O4 and H22B···O2. It is notable that the potential acceptor O3 is not involved in any hydrogen bonding interactions.

Conclusions

The formation of two- and three-dimensional networks of classical hydrogen bonds is strongly dependent upon the number of hydrogen bond donors; in compounds **2** and **3**, the availability of only two
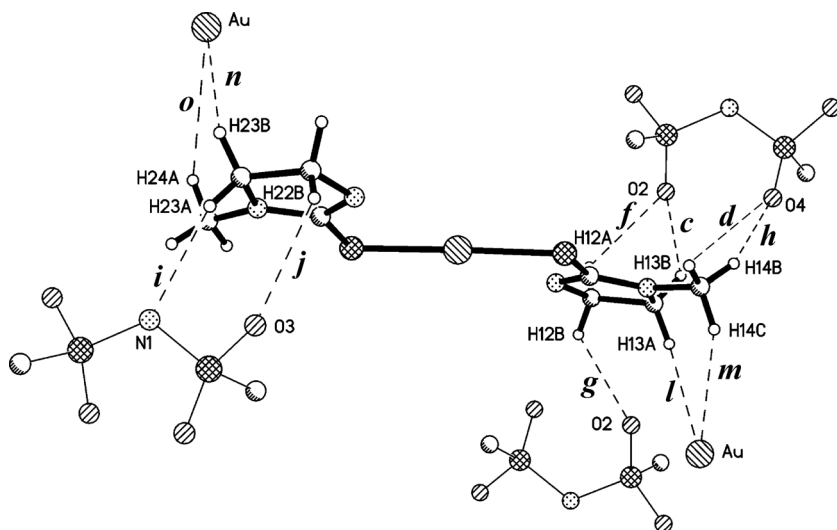

Fig. 12. Compound **2**, weak hydrogen bonds from one cation to adjacent anions and cations. The contact H23B···O3#7 (2.67 Å) has been omitted for clarity, because a further anion would have to be included; it may be noted that H23B thereby becomes a donor in a three-centre system (to Au and O3).

classical hydrogen bond donors gives rise to the formation of a chain and discrete rings, respectively, whereas compound **1**, which has twice as many classical hydrogen bond donors, forms thick layers, by connecting the chains, consisting of two classical hydrogen bonds, with ring patterns, formed by two additional classical hydrogen bonds. A similar result was obtained for the chloride salts of the bis(thione)gold(I) cations [3]. In contrast to the chlorides, however, the much larger DMS anions cause an additional restriction with respect to the conformation of the thione ligands; whereas in hydrated and anhydrous bis(imidazolidine-2-thione)gold(I) chloride the thione ligands showed a *cis* or staggered arrangement respectively, giving rise to the formation of small ring structures, the amide salts crystallise in the sterically favoured *trans*-formation. The most striking similarity with the chloride salts is found in the formation of "hairpin bends" in chains that can be regarded as topologically analogous with respect to the hydrogen bonds (*i.e.* the $C_2^2(14)$ chain formed by compound **3** is directly transformable into the $C_2^1(10)$ chains in both bis(Me-etu)gold(I) chloride [3] and bis(Pr-etu)gold(I) chloride [6] through representation of the amide anion as a single hydrogen bond acceptor entity, *cf.* Fig. 6). Compound **3** illustrates that the *exo* (farther from the gold atom) NH groups lead to a completely different network of classical hydrogen bonds, mainly based on the formation of discrete rings, connected non-classical hydrogen bonds, Au···S and S···S interactions.

Experimental Section

Physical measurements

These were recorded as described in [3].

Preparations

The compounds L_2Au^+ DMS^- were prepared from the corresponding chloride salts as follows: 1 mmol of the chloride salt was dissolved in 50 ml of ethanol (tht) or suspended in 30 ml of methanol (Me-tht or tzt derivatives) and treated with a solution of silver dimesylamide (1 mmol; kindly provided by Prof. A. Blaschette) in acetonitrile (5 ml). The cloudy reaction mixture was stirred for 1.5 h at room temperature with the exclusion of light. After filtering off the precipitated AgCl, the colourless filtrate was stored at $-18\ ^\circ$C for 12 h. to yield crystals of L_2Au^+ DMS^-.

Bis(imidazolidine-2-thione)gold(I) di(methanesulfonyl)amide (1)

Yield: 0.366 g (64%). – Dec. > 144 °C. – ^{1}H NMR (d$_6$-DMSO): $\delta = 2.72$ (6H, s; CH$_3$), 3.75 (8H, s; CH$_2$), 9.30 (4H,

bs; NH) – MS (gly): FAB (neg.; A = anion) $m/z = 171$ (8%, [A − H]$^-$), 172 (100%, [A]$^-$), 540 (2%, [Au + 2A − H]$^-$); FAB (pos.) $m/z = 103$ (4%, [K − Au(C$_3$H$_6$N$_2$S)+H]$^+$), 299 (4%, [K − (C$_3$H$_4$N$_2$S)]$^+$), 399 (4%, [K − 2H]$^-$), 401 (35%, [K]$^+$), 402 (6%, [K + H]$^+$),

699 (2%, [2K−(C$_3$H$_6$N$_2$S)−H]$^+$). – C$_8$H$_{18}$AuN$_5$O$_4$S$_4$ (573.52): calcd. C 16.75, H 3.17, N 12.21, S 22.36; found C 16.81, H 3.33, N 12.30, S 21.94.

Bis(1-methyl-imidazolidine-2-thione)gold(I) di(methanesulfonyl)amide (2)

Yield: 0.196 g (65%). – Dec. > 161 °C. – ^{1}H NMR (d$_6$-DMSO): $\delta = 2.72$ (6H, s; CH$_3$), 3.06 (6H, s; NCH$_3$), 3.63 (4H, m, 2nd order spectrum of *ABNM* spin system; CH$_2$), 3.86 (4H, m, 2nd order spectrum of *ABNM* spin system; CH$_2$), 9.10 (2H, bs; NH). – MS (NBA): FAB (neg.) $m/z = 172$ (100%, [A]$^-$); FAB (pos.) $m/z = 115$ (10%, [K − Au(CH$_3$-C$_3$H$_6$N$_2$S)−H]$^+$), 313 (19%, [K−(CH$_3$-C$_3$H$_6$N$_2$S)]$^+$), 427 (13%, [K − 2H]$^+$), 429 (100%, [K]$^+$), 741 (4%, [2K−(CH$_3$-C$_3$H$_6$N$_2$S)]$^+$). – C$_{10}$H$_{22}$AuN$_5$O$_4$S$_4$ (601.66): calcd. C 19.96, H 3.69, N 11.64, S 21.32; found C 19.95, H 3.70, N 11.55, S 21.39.

Bis(1,3-thiazolidine-2-thione)gold(I) di(methanesulfonyl)amide (3)

Yield: 0.075 g (18%). – M.p.: 142 °C. – ^{1}H NMR (d$_6$-DMSO): $\delta = 2.80$ (6H, s; CH$_3$), 3.68 (4H, t, ^3J(H − H) = 8.4 Hz; CH$_2$), 4.22 (4H, t, ^3J(H − H) = 8.4 Hz; CH$_2$). – MS (NBA): FAB (neg.) $m/z = 172$ (100%, [A]$^-$); FAB (pos.)= 316(6%, [K−(C$_3$H$_6$NS$_2$)]$^+$), 435 (100%, [K]$^+$), 437 (14%, [K + 2H]$^+$), 750 (8%, [2K−(C$_3$H$_6$NS$_2$)−H]$^+$), 752 (6%, [2K−(C$_3$H$_6$NS$_2$)+H]$^+$). – C$_8$H$_{16}$AuN$_3$O$_4$S$_6$ (607.68): calcd. C 15.81, H 2.66, N 6.92; S 31.66; found C 15.42, H .86, N 6.74, S 32.02.

X-ray structure determinations: The crystals were mounted in inert oil on glass fibres. Data were measured using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) on *Siemens* P4 (**1,2**) or *Bruker* SMART 1000 CCD diffractometers (**3**), fitted with low temperature attachments. Structures were refined anisotropically on F^2 [8]. 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. *Hydrogen atom treatment:* Hydrogen atoms bonded to nitrogen atoms were located in Fourier syntheses and refined freely; for compound **3**, N−H distances were restrained to be equal using the *SADI* instruction [8]. These H atoms cannot be geometrically positioned with certainty because their parent nitrogen atoms cannot be assumed to have a planar substituent geometry. Methyl hydrogens were located in difference syntheses, idealised and refined as rigid groups allowed to rotate but not to tip. Other hydrogen atoms were placed in calculated positions and refined using a riding model.

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 (and those $< 120°$ always) 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-232249 (**1**), 232250 (**2**) and 232251 (**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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