Secondary Interactions in Gold(I) Complexes with Thione Ligands. 1. Three Ionic Chlorides

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Dedicated to Prof. Dr. José Vicente on the occasion of his 60th birthday

Secondary interactions in the structures of $[(etu)_2Au]^+Cl^- \cdot H_2O$ (**1**), $[(etu)_2Au]^+Cl^-$ (**2**) and $[(Me-etu)_2Au]^+Cl^-$ (**3**) (etu = imidazolidine-2-thione) have been analysed. Within the cations, the torsion angle C-S···S-C is effectively the sole degree of freedom, and varies from almost eclipsed for **1** ($-20°$) *via* $-79°$ for **2** to exactly $180°$ in **3**. Both **1** and **2** form ten-membered rings in which the water molecule or the chloride ion respectively act as hydrogen bond acceptor to two NH donors of the cation. Further classical hydrogen bonds lead to the formation of double layer structures. Compound **3**, in which the gold atom lies on an inversion centre and the chloride on a twofold axis, utilises its one N-H···Cl contact to form chains of hairpin bends, with Au···Cl contacts in the chain direction. Weak hydrogen bonds C-H···Cl and C-H···Au play at best a minor role in **1**, but are more pronounced in **2** and **3**.

Key words: Aurophilicity, Thiones, Gold, Hydrogen Bonds, Secondary Interactions

Introduction

We are interested in secondary interactions in gold(I) complexes and have recently published a series of studies of hydrogen bonding in amine complexes of gold(I) [1]. We have now extended our studies to gold(I) complexes involving heterocyclic ligands bearing a thione group, which as a soft donor preferentially co-ordinates to the gold atom. In an attempt to investigate the influences of hydrogen bond donors and acceptors on the crystal packing, we have synthesised different combinations of cations and anions. The three cations $[L_2Au]^+$ with L = imidazolidine-2-thione ("ethylenethiourea", etu), 1-methyl-imidazolidine-2-thione (Me-etu) and thiazolidine-2-thione (tzt) differ in the number of classical hydrogen bond donors (NH groups; 2, 1 and 1 per ligand, respectively). The anions are either the small and sterically undemanding chloride, the large and optically active camphorsulfonate, or various disulfonylamides, which are well-known as versatile hydrogen bond acceptors [1].

In the first part of a short series of publications, we report here the synthesis and low temperature structures of the chlorides $[(etu)_2Au]^+Cl^- \cdot H_2O$ (**1**),

etu   Me-etu   tzt
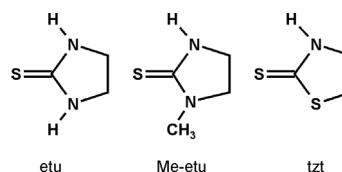
$[(etu)_2Au]^+Cl^-$ (**2**) and $[(Me-etu)_2Au]^+Cl^-$ (**3**). The structure of compound **1** is a redetermination of our earlier room temperature structure [2], in which however the water hydrogens were not located and for which no detailed analysis of the hydrogen bonding pattern was presented. There are two related structures in the literature: $[(tzt)_2Au]^+Cl^- \cdot H_2O$ [3] and $[(^iPr-etu)_2Au]^+Cl^-$ [4].

All the crystallographically characterised complexes display complex hydrogen bonding networks. Qualitative comparisons of the individual patterns are presented on the basis of graph theoretical analysis [5].

Discussion

The compounds $[(etu)_2Au]^+Cl^- \cdot H_2O$ (**1**, Fig. 1) and $[(etu)_2Au]^+Cl^-$ (**2**, Fig. 2) crystallise with one for-
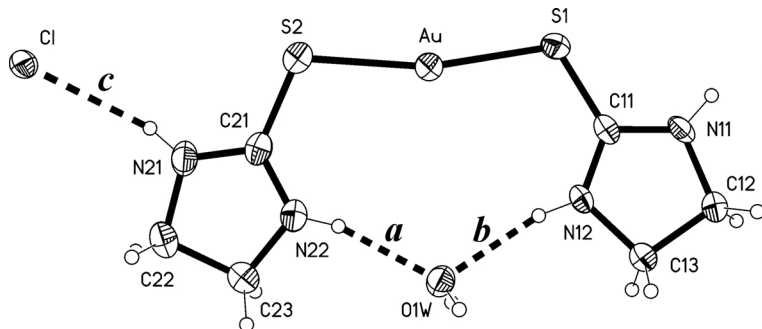
Fig. 1. Bis(imidazolidine-2-thione)gold(I) chloride monohydrate (**1**), asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds. Here and in the other Figures, hydrogen bonds are labelled with italic letters corresponding to Table 1.

Table 1. Hydrogen bonds in **1**, **2** and **3**.

Bond	d(D-H) [Å]	d(H…A) [Å]	d(D…A) [Å]	∠(DHA)
Compound 1:				
a: N22-H22···O1W	0.80(3)	2.01(3)	2.789(5)	165(2)
b: N12-H12···O1W	0.80(3)	2.06(3)	2.840(5)	167(2)
c: N21-H21···Cl	0.79(3)	2.40(3)	3.177(4)	165(3)
d: N11-H11···Cl[iii]	0.79(3)	2.42(4)	3.201(4)	168(5)
e: O1W-H01···.Cl[i]	0.80(5)	2.36(5)	3.146(3)	164(7)
f: O1W-H02···Cl[ii]	0.81(5)	2.37(5)	3.152(3)	163(7)
Compound 2:				
a: N21-H21···Cl	0.84(2)	2.42(3)	3.255(14)	173(14)
b: N11-H11···Cl	0.85(2)	2.33(5)	3.154(16)	164(12)
c: N12-H12···Cl[iv]	0.85(2)	2.35(3)	3.195(13)	170(6)
d: N22-H22···Cl2[v]	0.85(2)	2.40(3)	3.222(14)	163(10)
e: C12-H12A···Cl[vi]	1.08	2.70	3.59(2)	140
f: C13-H13B···Au[iv]	1.08	2.93	3.87(2)	145
Compound 3:				
a: N11-H11···Cl	0.80(5)	2.40(5)	3.160(4)	159(5)
b: C14-H14B···Cl[viii]	1.08	2.74	3.790(5)	165
c: C13-H13A···Cl[vii]	1.08	2.84	3.770(5)	145
d: C14-H14C···Au[vii]	1.08	2.80	3.789(5)	152
e: C13-H13A···Au[vii]	1.08	3.09	3.982(4)	140

Symmetry transformations for equivalent atoms: [i] $x, y, z-1$; [ii] $-x+2, -y+1, -z+1$; [iii] $x-1, y, z-1$; [iv] $x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; [v] $-x+\frac{1}{2}, y-\frac{1}{2}, z$; [vi] $x+\frac{1}{2}, y, -z+\frac{1}{2}$; [vii] $x+\frac{1}{2}, y+\frac{1}{2}, z$; [viii] $-x+1\frac{1}{2}, -y+\frac{1}{2}, -z+1$.
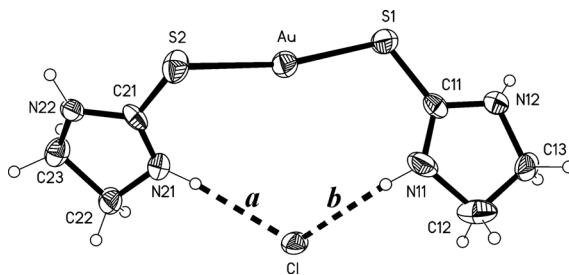
Fig. 2. Bis(imidazolidine-2-thione)gold(I) chloride (**2**), asymmetric unit with numbering scheme; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds.
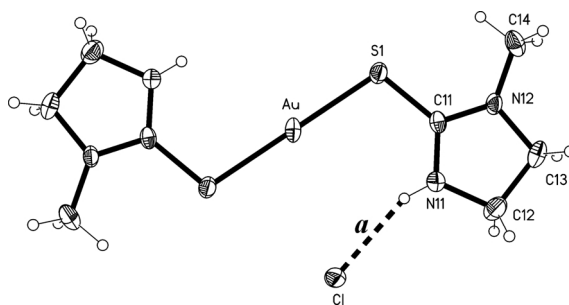
Fig. 3. Bis(1-methyl-imidazolidine-2-thione)gold(I) chloride (**3**), formula unit with numbering scheme of asymmetric unit; thermal ellipsoids are shown with 50% probability; hydrogen radii are arbitrary; dashed lines represent hydrogen bonds.

mula unit in the asymmetric unit. Compound [(Me-etu)$_2$Au]$^+$Cl$^-$ (**3**, Fig. 3) crystallises with half a formula unit in the asymmetric unit; the gold atom lies on an inversion centre and the chloride on a twofold axis.

The Au–S bond lengths of 2.2853(12), 2.2882(12) Å (**1**), 2.279(5), 2.296(5) Å (**2**) and 2.2951(11) Å (**3**) are similar to those in [(tzt)$_2$Au]$^+$ Cl$^-$·H$_2$O (2.281(5), 2.288(5) Å) [3] and may be regarded as normal. The S–C distances of 1.716(4), 1.715(5) Å (**1**), 1.710(16), 1.713(18) Å (**2**) and 1.722(4) Å (**3**) are slightly shorter than typical S–C single bonds (1.819 Å), but significantly longer than S–C double bonds (*ca.* 1.60 Å) [6]. The free ligand imidazolidine-2-thione (etu) shows an

S–C bond length of 1.694(3) Å [7]; the S–C bond elongation on co-ordination to gold has been observed previously [3].

The S–Au–S bond angles in complexes **1**, 166.95(4)° and **2**, 169.22(15)°, are significantly distorted from the linear co-ordination usually observed for gold(I). This may be attributed to bifurcated hydrogen bonds within the formula unit, which are formed between the two N–H hydrogens and (in
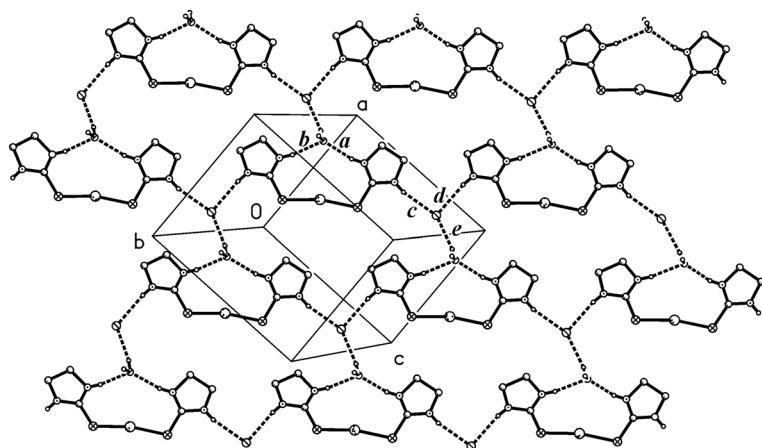
Fig. 4. Bis(imidazolidine-2-thione)gold(I) chloride monohydrate (**1**), single layer structure viewed perpendicular to the *xz* plane; atom radii are arbitrary; dashed lines represent hydrogen bonds; hydrogen atoms not involved in hydrogen bonding are omitted for clarity.
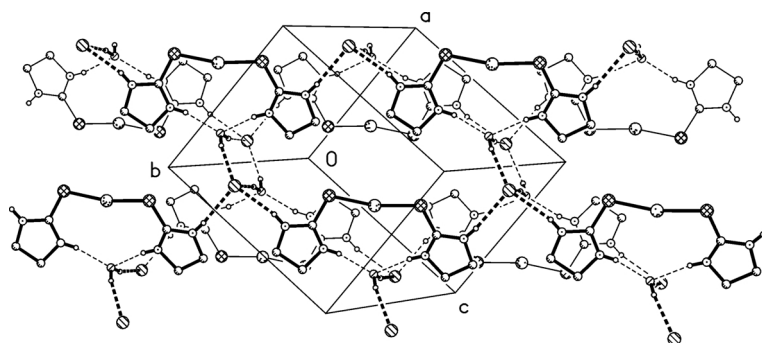

Fig. 5. Bis(imidazolidine-2-thione)gold(I) chloride monohydrate (**1**), double layer structure viewed perpendicular to the *xz* plane; atom radii are arbitrary; dashed lines represent hydrogen bonds; hydrogen atoms not involved in hydrogen bonding are omitted for clarity. The lower half of the layer is depth coded with thinner bonds.

complex **1**) the water oxygen atom or (in complex **2**) the chloride anion (Figs. 1 – 2, Table 1). The rings thus formed can be described as $R_2^1(10)$ at the binary level (*i.e.* $N_2(a,b)$ in both **1** and **2**); the ring is approximately planar for **1** but not for **2** (mean deviations 0.09, 0.38 Å). The hydrogen bonds also have an effect on the conformation of the ligands in both complexes **1** and **2**, giving rise to sterically disadvantageous *cis* arrangements of the etu rings. Nevertheless, the resulting C–S···S–C torsion angles in both complexes are different: the arrangement of the ligands in **1** is approximately eclipsed (torsion angle C–S···S–C $-20.1(2)°$) and parallel, whereas in **2** it is staggered (C–S···S–C $-79.0(8)°$). This difference is associated with the non-planarity of the ten-membered ring in **2**, but could also be ascribed to the different properties of the respective hydrogen bond acceptors; the chloride anion is a larger and weaker hydrogen bond acceptor than the oxygen atom, which therefore forms shorter hydrogen bonds (Table 1). An alternative explanation can be sought in the crystal packing (see below).

The C-S-Au angle seems to be a fairly "soft" parameter; nonetheless, we note that the angles in **1** and

2 (106 – 110°) lie towards the upper end of the normal range of *ca.* 101 – 110° and surmise that this is associated with the formation of the ten-membered rings.

Because of the imposed symmetry, the S–Au–S axis in **3** shows ideal linearity at gold and an antiperiplanar *trans* conformation of the ligands (C–S···S^i–C^i 180.0°). Its C-S-Au angle is somewhat less than the mean value in **1** and **2**.

The heterocyclic rings are approximately planar (mean deviation 0.02, 0.07 Å for **1**, 0.04, 0.10 Å for **2**, 0.02 Å for **3**), with the less planar ring in **1** and **2** exhibiting a greatly flattened C_2 (twist) conformation through the *ipso* C atom. The gold atoms are also approximately coplanar with the rings (for Au-S-C-N torsion angles, see Tables). Thus, despite the apparent high degree of flexibility of the ligands, the only parameter that changes significantly from one structure to another is the S-C···C-S torsion angle.

The crystal packing is primarily determined by classical hydrogen bonds. In compound **1**, the chloride anion accepts four classical hydrogen bonds, two from NH groups and two from water OH. Three of these link the $R_2^1(10)$ rings to form a layer parallel
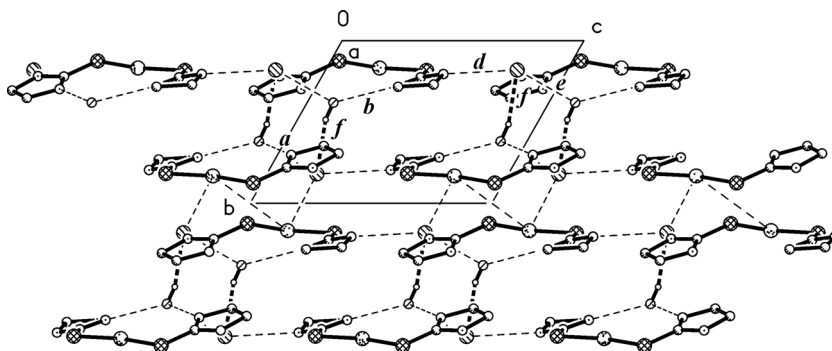
Fig. 6. Bis(imidazolidine-2-thione)gold(I) chloride monohydrate (**1**), two double layers projected parallel to the *x* axis; atom radii are arbitrary. The thick dashed lines represent hydrogen bonds O-H···Cl connecting the two single layers; other hydrogen atoms are omitted for clarity. Other hydrogen bonds are represented by thin lines, as are the Au...Au and Au...Cl contacts between double layers.
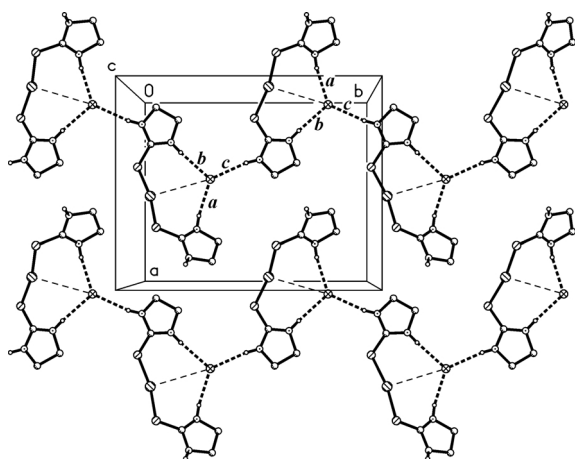

Fig. 7. Bis(imidazolidine-2-thione)gold(I) chloride (**2**), single layer structure viewed parallel to the *z* axis; atom radii are arbitrary; thick dashed lines represent hydrogen bonds, thin dashed lines the Au···Cl contacts; hydrogen atoms not involved in hydrogen bonding are omitted for clarity.
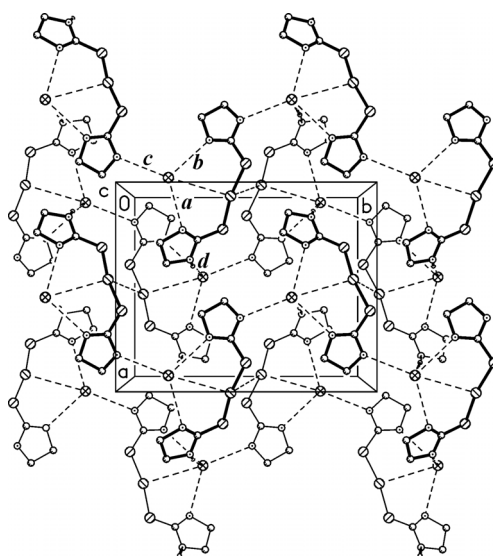

Fig. 8. Bis(imidazolidine-2-thione)gold(I) chloride (**2**), double layer structure viewed parallel to the *z* axis; atom radii are arbitrary; dashed lines represent hydrogen bonds; only those hydrogen atoms linking the two single layers are shown. The lower half of the layer is depth coded with thinner bonds.

to the *xz* plane (Fig. 4), whereby the chloride anion forms one link of chains with overall direction parallel to [101], described at the binary level by the graph set $C_2^1(10)$ (Fig. 4), thus yielding the complex graph set $C_4^2(12)[R_2^1(10)]$. The fourth hydrogen bond connects two inversion-related layers to give double layers (Fig. 5), thereby forming "squares" $[(H_2O)_2(Cl^-)_2]$ at $0,\frac{1}{2},0$ with the graph set $R_2^2(6)$.

The presence of classical hydrogen bond donors and acceptors is not an automatic bar to "weak" hydrogen bonds [8]. In **1**, however, there are no C–H···Cl contacts < 2.89 Å. In the presence of several classical hydro-

gen bonds, we assume that such contacts, corresponding approximately to the sum of the van der Waals radii (2.95 Å), play at best a subordinate role in the packing. There are also no particularly short Au···Au contacts; the shortest such is 4.3859(8) Å between adjacent double layers, which are also linked by the contact Au···Cl 3.5471(12) Å (Fig. 6).

In the anhydrous complex **2**, the packing is similar to that of **1** despite the lack of a water molecule, and
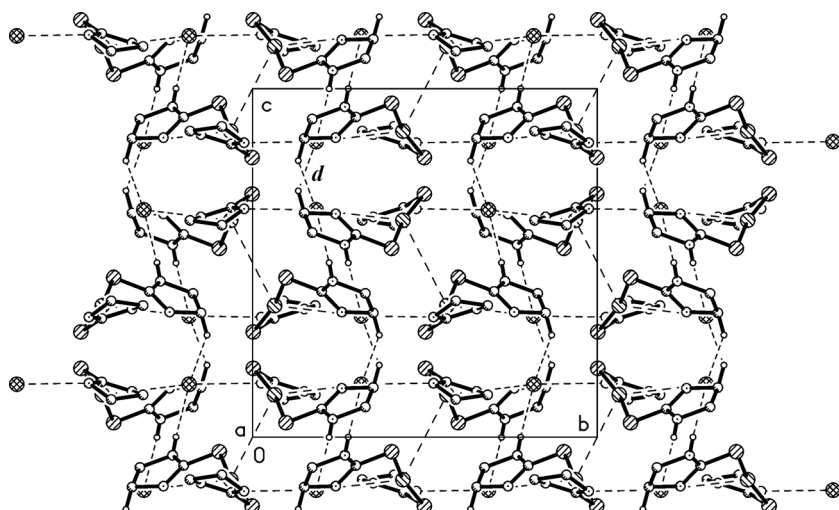
Fig. 9. Bis(imidazolidine-2-thione)gold(I) chloride (**2**), three double layers projected parallel to the x axis; atom radii are arbitrary. The thin dashed lines represent secondary interactions N···Cl (within single layers), N-H···Cl and Au···Au (connecting the two single layers), and C-H···Cl (connecting the double layers); other hydrogen atoms are omitted for clarity.

again consists of double layers. The chloride anion accepts four classical hydrogen bonds, one from each NH donor. Three of these, as in **1**, link the $R_2^1(10)$ rings to form a layer, here parallel to the xy plane (Fig. 7); the layer consists of chains of molecules, parallel to the y axis and propagated by the b glide plane. At the binary level, this chain can be described by the graph set $N_2(b,c) = C_2^1(6)$, yielding a complex graph set of the notation $C_4^2(16)[R_2^1(10)][N_3(a,b,c)]$. The fourth hydrogen bond connects two such layers *via* the 2_1 axis parallel to x to form double layers (Figs. 8, 9). Because there is no water molecule, suitably angled at the oxygen atom, to mediate the hydrogen bonds between the two halves of the double layer, the chloride itself must adopt the role of catering for the third dimension, and therefore one heterocyclic ring must be appreciably tilted with respect to the layer plane.

Several non-classical contacts are also observed in **2**. The long and presumably weak contacts Au···Au 4.0718(13) Å and Au···Cl 3.778(4) Å lie within the double layer or within the asymmetric unit, respectively. More significantly, adjacent double layers are connected by C-H···Cl contacts of only 2.70 Å (Fig. 9). Finally, one must consider the possibility that the electronegative metal gold can act as a hydrogen bond acceptor, even from C-H bonds [9]. The two contacts H13A···Au and H13B···Au within the single layers are quite long (3.35, 3.12 Å), have very narrow angles at hydrogen (92, 105°), and indeed seem to repel the gold atoms (*cf.* Fig. 7), but a second H13B···Au contact between the two components of the double layer (2.93 Å, 145°) may well represent an additional stabilising fac-
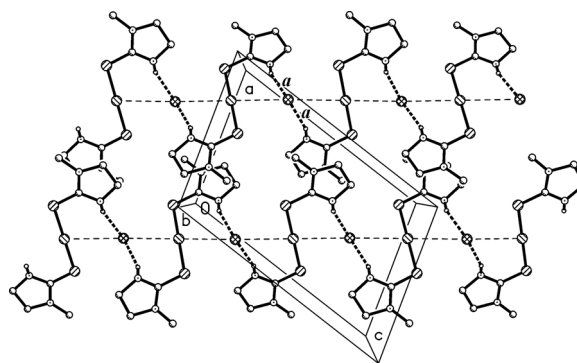

Fig. 10. Bis(1-methyl-imidazolidine-2-thione)gold(I) chloride (**3**), two chains viewed parallel to the y axis; atom radii are arbitrary; dashed lines represent hydrogen bonds (thick) or Au···Cl contacts (thin); hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

tor. This contact is not shown in the various Figures for reasons of clarity.

In compound **3**, the blocking of one classical hydrogen bond donor by a methyl group must have a major effect on the packing. It would still be possible for an $R_2^1(10)$ ten-membered ring, as in **1** and **2**, to be formed, but this does not prove to be the case. The asymmetric unit contains only one NH donor and one chloride acceptor, and the one classical hydrogen bond thus formed leads to chains consisting of a series of "hairpin bends", but with overall direction parallel to [101], described at the unitary level by the graph set $C_2^1(10)$ (*i.e.* $N_1(a) = C_2^1(10)$) (Fig. 10). The Au···Cl contacts within the chains are at 3.4965(5) Å rather shorter than in **1**
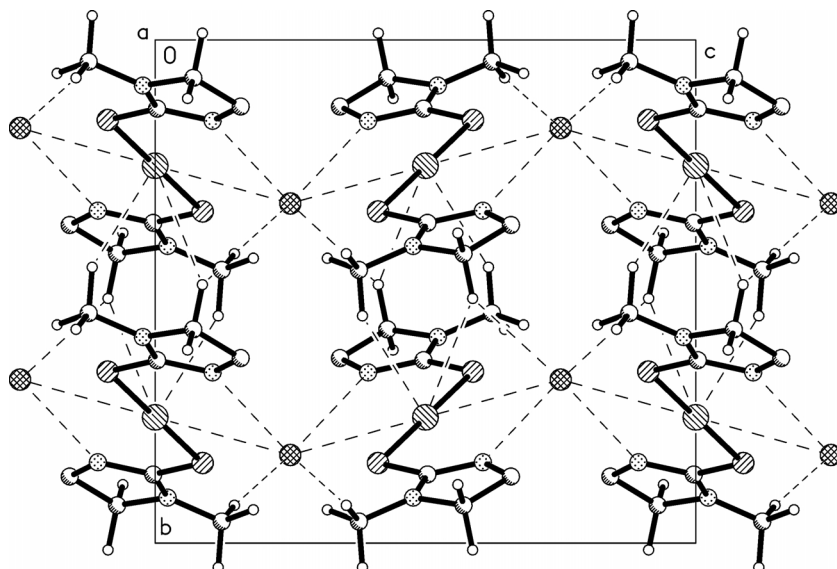
Fig. 11. Bis(1-methyl-imidazolidine-2-thione)gold(I) chloride (**3**) projected parallel to the *x* axis; atom radii are arbitrary; thin dashed lines represent hydrogen bonds (including C-H···Au and CH···Cl) or Au···Cl contacts. Hydrogens of NH groups are omitted.
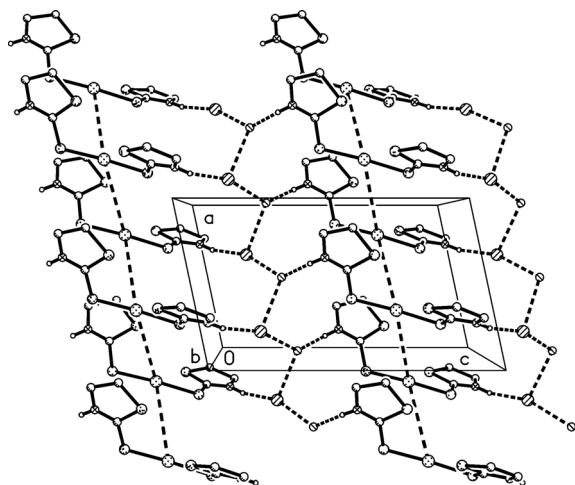

Fig. 12. Packing diagram of bis(1,3-thiazolidine-2-thione)gold(I) chloride hydrate viewed parallel to the *y* axis. Hydrogen bonds N-H···Cl and O···Cl are indicated by dashed lines, as are the long Au···Au contacts (see text). The diagram is based on the deposited coordinates from ref. [3].

Fig. 13. Packing diagram of bis(N-propyl-1,3-thiazolidine-2-thione)gold(I) chloride; one chain viewed parallel to the *y* axis. Hydrogen bonds N-H···Cl are indicated by thick dashed lines, Au···Cl contacts by thin dashed lines (see text). The diagram is based on the deposited coordinates from ref. [4].

and **2**; the S...Cl contact of 3.5572(11) Å within the chain may simply be imposed by the hairpin geometry. Contacts between chains (Fig. 11) involve two C-H···Cl and two C-H···Au contacts, one of the latter being as short as 2.80 Å (the methyl hydrogens in question were identifiable in difference Fourier syntheses).

Because the extended packing diagrams of $[(tzt)_2Au]^+Cl^-·H_2O$ [3] and $[(^iPr\text{-}etu)_2Au]^+Cl^-$ [4]

were not presented in the original publications, we describe them briefly here, based on coordinates extracted from the Cambridge Database [10]. The former, with a S-C···C-S torsion angle of $-40.1°$, is a layer structure (Fig. 12) in which ribbons of cations with approximately parallel S-Au-S axes are con-

Compound	1	2	3
Formula	$C_6H_{14}AuClN_4OS_2$	$C_6H_{12}AuClN_4S_2$	$C_8H_{16}AuClN_4S_2$
M_r [g/mol]	454.75	436.73	464.78
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P(-1)$	$Pbca$	$C2/c$
Cell dimensions	$a = 8.8006(14)$	$a = 11.499(3)$	$a = 8.7398(10)$
[Å, °]	$b = 8.9544(12)$	$b = 14.305(3)$	$b = 11.7877(14)$
	$c = 10.3864(16)$	$c = 14.476(3)$	$c = 13.2514(18)$
	$\alpha = 115.153(10)$	$\alpha = 90$	$\alpha = 90$
	$\beta = 92.054(14)$	$\beta = 90$	$\beta = 107.296(10)$
	$\gamma = 116.303(10)$	$\gamma = 90$	$\gamma = 90$
V [Å^3]	638.32(17)	2381.3(9)	1303.5(3)
Z	2	8	4
Crystal habit	Colourless prism	Colourless plate	Colourless prism
Crystal size [mm^3]	$0.48 \times 0.10 \times 0.10$	$0.50 \times 0.30 \times 0.06$	$0.19 \times 0.14 \times 0.13$
D_x [Mg/m^3]	2.366	2.436	2.368
θ Range [°]	3.12 to 27.50	3.18 to 25.00	3.03 to 25.00
μ [mm^{-1}]	12.04	12.90	11.79
Temperature [K]	173	173	173
Absorption correction	Empirical (SHELXA)	ψ-scans	ψ-scans
T_{max}/T_{min}	0.827 / 0.468	0.687 / 0.161	0.904 / 0.687
Measured refls	4008	2625	2334
Independent refls	2715	2086	1147
R_{int}	0.0173	0.0327	0.0194
$F(000)$	428	1632	880
Restraints	55	52	13
Parameters	160	139	80
S	1.070	0.904	0.917
$R1[F^2 > 2\sigma(F^2)]$	0.0201	0.0560	0.0174
$wR2(F^2,$ all refl.)	0.0459	0.1487	0.0405
$\Delta\rho_{min}/\Delta\rho_{max}$ [eÅ^{-3}]	0.823 / −0.900	2.028 / −2.535	0.917 / −0.835

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

nected by hydrogen bonds N-H···Cl and N-H···O (one of each type) to an infinite zigzag chain of alternating waters and chlorides. The Au...Au contacts between cations are at 4.44 Å very long, but are shown in the Figure. In [(^{i}Pr-etu)$_2$Au]$^+$Cl$^-$ (Fig. 13), where the ligands are antiperiplanar (S-C···C-S 165.1°), chains topologically identical to those of **3** are formed, in which the Au···Cl contacts are 3.42 and 3.80 Å. Clearly it would be interesting to determine the structure of anhydrous [(tzt)$_2$Au]$^+$Cl$^-$ for comparison, but we were unable to obtain suitable crystals.

Comparison of the hydrogen bonding networks in **1**, **2** and **3** leads to the following conclusions: The two- and three-dimensional patterns of classical hydrogen bonds are influenced rather by the number of hydrogen bond donors than by the number of acceptors. In spite of the additional H$_2$O molecule, the packing of **1** reveals ring, layer and double layer patterns similar to those in **2**. Substitution of two N–H hydrogen atoms in **3** has blocked, predictably, the formation of a three-dimensional network of N–H···Cl bonds and, less predictably, the $R_2^1(10)$ ring substructure. Non-classical hydrogen bonds C-H···Cl and even C-H···Au play a role

in the anhydrous structures. The list of potential contacts is however still longer; we have not considered C-H···S or Au···N contacts explicitly, because they are quite long (the shortest are C-H···S *ca.* 2.90 Å in all three structures and Au···N *ca.* 3.6 Å in **1** and **2**). Further publications in this series will reveal a more significant role for these contacts in structures where classical hydrogen bonds do not predominate to the same extent.

Experimental Section

Physical measurements

^{1}H NMR spectra were recorded on a *Bruker* AC 200 spectrometer (Frequencies: ^{1}H: 200.1 MHz, ^{13}C: 50.3 MHz), ^{13}C NMR and ^{13}C–^{1}H NMR correlation spectra were recorded on a *Bruker* AM 400 spectrometer (Frequencies: ^{1}H: 400.1 MHz, ^{13}C: 100.6). All NMR measurements were carried out in d$_6$-DMSO and referenced with TMS ($\delta = 0$) as internal standard. Mass spectra were recorded on a *Finnigan* MAT 8430, using the FAB method (Matrix: NBA, unless stated otherwise). The measurement of melting points and decomposition temperatures was carried out on a *Büchi* 510.

Table 3. Bond lengths [Å], bond angles and torsion angles [°] in **1**.

Au-S(1)	2.2853(12)	C(13)-N(12)	1.470(5)
Au-S(2)	2.2882(12)	S(2)-C(21)	1.715(5)
S(1)-C(11)	1.716(4)	C(21)-N(22)	1.312(5)
C(11)-N(12)	1.310(5)	C(21)-N(21)	1.328(6)
C(11)-N(11)	1.324(5)	N(21)-C(22)	1.461(6)
N(11)-C(12)	1.467(5)	C(22)-C(23)	1.536(6)
C(12)-C(13)	1.536(6)	C(23)-N(22)	1.460(6)
S(1)-Au-S(2)	166.95(4)	C(21)-S(2)-Au	109.60(14)
C(11)-S(1)-Au	110.18(14)	N(22)-C(21)-N(21)	110.4(4)
N(12)-C(11)-N(11)	111.1(4)	N(22)-C(21)-S(2)	127.9(3)
N(12)-C(11)-S(1)	128.5(3)	N(21)-C(21)-S(2)	121.6(3)
N(11)-C(11)-S(1)	120.4(3)	C(21)-N(21)-C(22)	111.3(4)
C(11)-N(11)-C(12)	111.5(3)	N(21)-C(22)-C(23)	101.7(4)
N(11)-C(12)-C(13)	102.7(3)	N(22)-C(23)-C(22)	101.7(3)
N(12)-C(13)-C(12)	102.2(3)	C(21)-N(22)-C(23)	111.7(4)
C(11)-N(12)-C(13)	112.2(3)		
C(11)-S(1)···S(2)-C(21)	−20.1(2)	Au-S(2)-C(21)-N(22)	13.7(4)
		Au-S(1)-C(11)-N(12)	4.2(4)

Table 4. Bond lengths [Å], bond angles and torsion angles [°] in **2**.

Au-S(1)	2.279(5)	C(13)-N(12)	1.465(19)
Au-S(2)	2.296(5)	S(2)-C(21)	1.713(18)
S(1)-C(11)	1.710(16)	C(21)-N(22)	1.32(2)
C(11)-N(11)	1.313(19)	C(21)-N(21)	1.322(19)
C(11)-N(12)	1.32(2)	N(21)-C(22)	1.43(2)
N(11)-C(12)	1.50(2)	C(22)-C(23)	1.53(2)
C(12)-C(13)	1.47(3)	C(23)-N(22)	1.50(2)
S(1)-Au-S(2)	169.22(15)	C(21)-S(2)-Au	106.2(5)
C(11)-S(1)-Au	108.5(6)	N(22)-C(21)-N(21)	108.6(16)
N(11)-C(11)-N(12)	110.3(15)	N(22)-C(21)-S(2)	122.8(12)
N(11)-C(11)-S(1)	128.4(13)	N(21)-C(21)-S(2)	128.6(14)
N(12)-C(11)-S(1)	121.2(12)	C(21)-N(21)-C(22)	112.7(14)
C(11)-N(11)-C(12)	111.7(15)	N(21)-C(22)-C(23)	101.4(14)
C(13)-C(12)-N(11)	100.9(13)	N(22)-C(23)-C(22)	99.4(13)
N(12)-C(13)-C(12)	106.0(15)	C(21)-N(22)-C(23)	111.0(12)
C(11)-N(12)-C(13)	110.1(14)		
C(11)-S(1)···S(2)-C(21)	−79.0(8)	Au-S(2)-C(21)-N(21)	31.6(16)
		Au-S(1)-C(11)-N(11)	6.6(16)

Preparations

Bis(imidazolidine-2-thione)gold(I) chloride (**1**)

A suspension of imidazolidine-2-thione (FLUKA, 18 mmol, 1.84 g) in deionised water (60 ml) was added to a stirred solution of $HAuCl_4 \cdot 3H_2O$ (3 mmol, 1.17 g) in ethanol (15 ml) to give a clear yellow solution. After stirring for 12 h at room temperature, the white precipitate was filtered off. Upon storing the filtrate at 4 °C colourless crystals of **1** separated. The product was filtered, washed with ethanol and dried *in vacuo* for 1 h. (Drying of **1** for 4 h *in vacuo* gives **2**.) Yield: 1.21 g (89%).

Dec. 114 °C (- H_2O). – M.p. 240 °C. – 1H-NMR (d_6–DMSO): $\delta = 3.68$ (8H, s; CH_2), 9.29 (4H, s; NH). – MS

Table 5. Bond lengths [Å], bond angles and torsion angles [°] in **3**.

Au-S(1)	2.2951(11)	N(11)-C(12)	1.455(6)
S(1)-C(11)	1.722(4)	C(12)-C(13)	1.530(7)
C(11)-N(11)	1.329(5)	C(13)-N(12)	1.471(6)
C(11)-N(12)	1.332(5)	N(12)-C(14)	1.433(6)
S(1)-Au-S(1)#1	180.0	N(11)-C(12)-C(13)	103.4(4)
C(11)-S(1)-Au	106.49(15)	N(12)-C(13)-C(12)	102.5(3)
N(11)-C(11)-N(12)	110.9(4)	C(11)-N(12)-C(14)	127.2(4)
N(11)-C(11)-S(1)	127.0(3)	C(11)-N(12)-C(13)	111.2(4)
N(12)-C(11)-S(1)	122.1(3)	C(14)-N(12)-C(13)	120.9(4)
C(11)-N(11)-C(12)	111.6(4)		
C(11)-S(1)···S(1)#1 -C(11)#1	180.0	Au-S(1)-C(11)-N(11)	−3.5(4)

Symmetry transformation for equivalent atoms: #1 $-x+\frac{1}{2}$, $-y+\frac{1}{2}$, $-z+1$.

(gly): (FAB neg.) $m/z = 399$ (6%, [cation – 2H]⁻); (FAB pos.) $m/z = 103$ (4%, [cation – $Au(C_3H_6N_2S)$ + H]⁺), 299 (3%, [cation – $(C_3H_4N_2S)$]⁺), 401 (33%, [cation]⁺). – $C_6H_{14}AuClN_4OS_2$ (454.80): calcd. C 15.85, H 3.11, N 12.32, S 14.10; found C 15.31, H 2.85, N 12.01, S 13.87.

Compounds **2** and **3** were synthesised from (tht)AuCl [11] and the respective ligand (imidazolidine-2-thione (FLUKA), **2**; 1-methyl-imidazolidine-2-thione (ACROS), **3**) by adding 1 mmol of solid ligand to a stirred solution of (tht)AuCl (0.5 mmol, 0.160 g) in acetonitrile (30 ml). After stirring the cloudy reaction mixture (4 h, **2**; 2 h, **3**), the white precipitate was filtered off, washed with acetonitrile and dried *in vacuo* for 1 h. Analysis values for **3** are poor, but were determined from the same sample of single crystals that was used for the structure determination.

Bis(imidazolidine-2-thione)gold(I) chloride (**2**)

Yield: 0.199 g (91%). – M.p. 236 °C. – ¹H-NMR (d_6–DMSO): $\delta = 3.68$ (8H, s; CH_2), 9.22 (4H, bs; NH). – MS (NBA): FAB (neg.) $m/z = 399$ (15%, [cation – 2H]⁻); FAB (pos.) $m/z = 299$ (20%, [cation – $(C_3H_4N_2S)$]⁺), 401 (100%, [cation]⁺), 402 (10%, [cation + H]⁺), 699 (4%, [2(cation) – $(C_3H_6N_2S)$ – H]⁺). – $C_6H_{12}AuClN_4S_2$ (436.78): calcd. C 16.49, H 2.72, N 12.83, S 14.63, Cl 8.12; found C 16.29, H 2.85, N 12.63, S 14.67, Cl 7.83.

Bis(1-methyl-imidazolidine-2-thione)gold(I) chloride (**3**)

Yield: 0.442 g (95%). – Dec. > 240 °C. – ¹H-NMR (d_6–DMSO): $\delta = 3.10$ (6H, s; NCH_3), 3.68 (4H, bs; CH_2), 3.86 (4H, bs; CH_2). – MS (NBA): FAB (pos) $m/z = 313$ (44%, [cation – $(CH_3-C_3H_6N_2S)$]⁺), 399 (6%, [cation – $2CH_3$]⁺), 427 (10%, [cation – 2H]⁺), 429 (89%, [cation]⁺), 741 (2%, [2(cation) – $(CH_3-C_3H_6N_2S)$]⁺). – $C_8H_{16}AuClN_4S_2$ (464.82): calcd. C 20.67, H 3.48, N 12.06, S 13.79, Cl 7.63; found C 19.00, H 3.12, N 10.25, S 11.50, Cl 8.41.

Single crystals were obtained for **1** by evaporation of an aqueous solution over phosphorus pentoxide in a desiccator; for **2** by diffusion of diethyl ether into an ethanol solution of the anhydrous compound; and for **3** by diffusion of diethyl ether into an acetonitrile solution.

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 a *Siemens* P4 diffractometer fitted with an LT-2 low temperature attachment. Structures were solved by the heavy-atom method and refined anisotropically on F^2 [12]. Hydrogen atoms bonded to nitrogen atoms were located in Fourier syntheses and refined freely, but with N−H and C(-N-)H dis-

tances (and O-H where applicable) restrained to be equal using the *SADI* instruction where possible [12]; these H atoms cannot be geometrically positioned with certainty because their parent nitrogen atoms do not in general have a planar substituent geometry. Other hydrogen atoms were placed in calculated positions and refined using a riding model.

To calculate hydrogen bond parameters, C-H bond lengths were normalised to 1.08 Å.

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC-218263 (**1**), 218264 (**2**) and 218265 (**3**). Copies may be requested free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (E-mail: deposit@ccdc.cam.ac.uk).

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