

Two thiourea-containing gold(I) complexes

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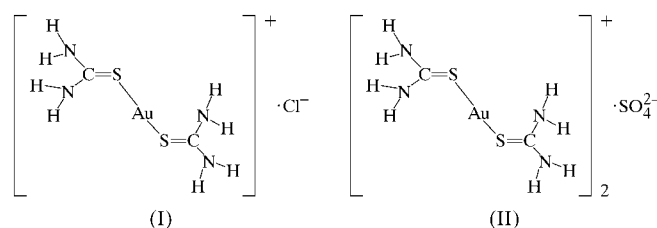
The crystal structures of two salts of bis(thiourea)gold(I) complexes, namely bis(thiourea- κ S)gold(I) chloride, $[\text{Au}(\text{CH}_4\text{N}_2\text{S})_2]\text{Cl}$, (I), and bis[bis(thiourea- κ S)gold(I)] sulfate, $[\text{Au}(\text{CH}_4\text{N}_2\text{S})_2]_2\text{SO}_4$, (II), have been determined. The chloride salt, (I), is isomorphous with the corresponding bromide salt, although there are differences in the bonding. The Au^{I} ion is located on an inversion centre and coordinated by two symmetry-related thiourea ligands through the lone pairs on their S atoms [Au–S 2.278 (2) Å and Au–S–C 105.3 (2)°]. The sulfate salt, (II), crystallizes with four independent $[\text{Au}(\text{CH}_4\text{N}_2\text{S})_2]^+$ cations per asymmetric unit, all with nearly linear S–Au–S bonding. The cations in (II) have similar conformations to that found for (I). The Au–S distances range from 2.276 (3) to 2.287 (3) Å and the Au–S–C angles from 173.5 (1) to 177.7 (1)°. These data are relevant in interpreting different electrochemical processes where gold–thiourea species are formed.

Comment

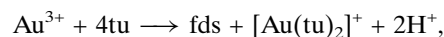
Thiourea (tu) is a complexing agent for a variety of transition metals (Gosavi & Rao, 1967; Bailey & Peterson, 1968; Porter *et al.*, 1992; Bott *et al.*, 1998; Piro *et al.*, 2000) and is employed in a number of electrochemical processes, such as copper electrodeposition, where it is used as an additive to produce smooth deposits, and as an inhibitor to prevent copper corrosion in aqueous environments. The study of these processes raises the issue of the possible formation and extent of participation of complex species in their kinetics and mechanisms. Recently, it was shown that several Cu^{I} –tu complexes, whose structures are now well established (Piro *et al.*, 2000), play a relevant role in copper corrosion and passivation in aqueous sulfuric acid (Haseeb *et al.*, 2001; Bolzán *et al.*, 2001). These findings open new horizons for the further investigation of electrochemical processes at solid electrodes

in the presence of organic additives, in order to discover new metal–additive complex structures and preparation procedures.

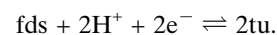
Electrochemical studies of gold electrodes in acidic tu-containing solutions have shown that soluble species are also formed during voltammetric scans in the potential range related to the thermodynamic stability of water (Bolzán *et al.*, 1999). These species are likely to be related to the formation of Au^{I} –tu complex ion species in solution. It has also been pointed out that the dissolution of the cationic Au^{I} complex formed, instead of the anionic complexes usually obtained by conventional dissolution methods for gold (Groenewald, 1975), may offer a novel approach to gold hydrometallurgy, as well as the use of acidic solutions of tu as a non-toxic alternative to cyanide for electropolishing. However, despite the apparent importance of Au–tu complexes in chemical and electrochemical processes, crystallographic and chemical data relating to Au–tu complexes are relatively scarce (Porter *et al.*, 1992) compared with those reported for Cu (Gash *et al.*, 1973; Griffith *et al.*, 1976, 1978; Ferrari & Gasparri, 1976; Bott *et al.*, 1998). Therefore, the determination of the structures of Au–tu complexes deserves further investigation in order to yield data relevant to the interpretation of the kinetics and mechanisms of electrochemical processes. To this end, the structures of bis(thiourea- κ S)gold(I) chloride, (I), and bis[bis(thiourea- κ S)gold(I)] sulfate, (II), are presented here.



From the preparation of the gold complexes, we noted the resemblance between the chemistry of Cu and Au in the presence of tu. In both cases, tu acts as a reducing agent, with subsequent formation of complex species where tu acts as the ligand. In the case of copper, Cu^{II} ions are reduced to Cu^{I} , forming complex species whose stoichiometry depends on the ratio between Cu^{I} and tu in solution (Piro *et al.*, 2000), whereas, in the case of gold, Au^{III} ions are reduced to Au^{I} by tu, thereby producing the soluble complex $[\text{Au}(\text{tu})_2]^+$. In this case, the corresponding electrochemical reaction can be written as



where fds is formamidine disulfide, the main product of the electro-oxidation of tu; it is produced according to the following redox reaction in acidic aqueous solutions (Szymaszek *et al.*, 1977):



This reaction is similar to that reported for the case of aqueous Cu^{II} and tu-containing solutions, where tu is oxidized by Cu^{II}

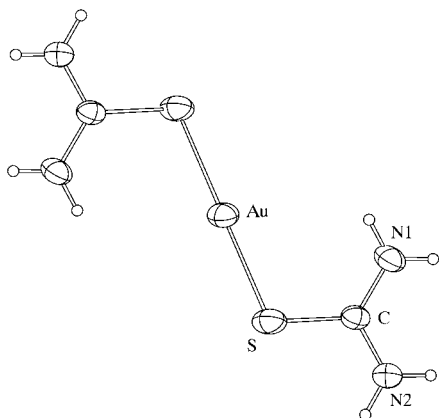


Figure 1

A view of the bis(tu)gold(I) cation in (I), showing the labelling of the atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

ions (Ratajczak & Pajdowski, 1974), yielding fds and $\text{Cu}^{\text{I}}\text{-tu}$ complex species (Javet & Hintermann, 1969).

Fig. 1 shows the bis(tu)gold(I) cation in (I). Although complex (I) is isomorphous with the bromide salt (Porter *et al.*, 1992), it has significant differences in the bond structure and these are discussed below.

The Au^{I} ion in (I) is sited at an inversion centre, coordinated to a pair of symmetry-related tu ligands through their S atoms [Au-S 2.278 (2) Å] *via* the sulfur electron lone pair [Au-S-C 105.3 (2)°], giving rise to perfectly linear S—Au—S bonding. The tu SCN_2 skeleton is planar within experimental error (the r.m.s. deviation of atoms from the least-squares plane is 0.004 Å) and it is twisted around the C—S vector, giving an Au—S—C—N1 torsion angle of 23.9 (6)°.

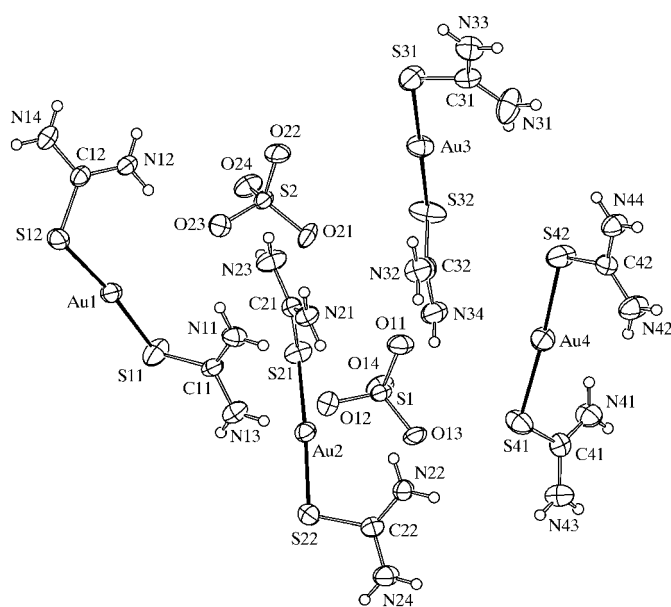


Figure 2

A view of the asymmetric unit of (II), showing the labelling of the atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The S—C bond distance is 1.718 (7) Å, in close agreement with the value of 1.72 (1) Å found in an X-ray crystal structure determination of free tu (Truter, 1967) and the value of 1.71 (1) Å determined in two neutron diffraction studies (Elcombe & Taylor, 1968; Mullen *et al.*, 1978). These values are shorter than the corresponding S—C bond length reported for $[\text{Au}(\text{tu})_2]\text{Br}$ [1.77 (1) Å; Porter *et al.*, 1992].

The C—N bond distances of 1.309 (8) and 1.294 (8) Å are equal within experimental accuracy, and are again in agreement with the corresponding values for free tu [$\text{C-N} = 1.34$ (1) and 1.33 (1) Å for the X-ray and neutron diffraction studies, respectively] and at variance with the unequal C—N distances of 1.26 (2) and 1.40 (2) Å reported for the bromide salt (Porter *et al.*, 1992).

Furthermore, the angles associated with the two sets of S—C—N atoms in (I) differ by about 5° [S-C-N1 123.0 (6)° and S-C-N2 117.9 (5)°], half the difference reported for the bromide salt.

The Cl^- ion, sited on a crystallographic twofold axis, is involved in a medium strength $\text{N-H}\cdots\text{Cl}$ interaction with the tu ligand [$\text{N}\cdots\text{Cl}$ 3.200 (7) Å and $\text{N-H}\cdots\text{Cl}$ 152°].

The asymmetric unit of (II) contains four independent $[\text{Au}(\text{tu})_2]^+$ complex cations (Fig. 2). In each, the Au^{I} ion is coordinated to two tu ligands through the S atoms [Au-S 2.276 (3)–2.287 (3) Å and Au-S-C 103.4 (4)–108.7 (3)°], forming nearly linear S—Au—S angles [173.5 (1)–177.7 (1)°]. These bond distances and angles are in agreement with the corresponding values found for (I) and the isomorphous bromide salt (Porter *et al.*, 1992).

The tu ligands of all four $[\text{Au}(\text{tu})_2]^+$ ions are planar within experimental error (r.m.s. deviation of atoms from the least-squares plane < 0.009 Å). The Au—S—C—N torsion angles vary from 4 (1) to 24.2 (9)°, while the dihedral angle between the pair of tu ligands of a given $[\text{Au}(\text{tu})_2]^+$ complex varies from 58.3 (3) to 85.1 (4)°.

The C—S and C—N bond lengths in (II) are in the ranges 1.71 (1)–1.76 (1) and 1.28 (1)–1.35 (1) Å, respectively. The shorter intermolecular $\text{Au}\cdots\text{Au}$ distance is 5.1379 (7) Å. The crystal of (II) is further stabilized by a net of medium to strong $\text{N-H}\cdots\text{O}$ hydrogen bonds; for the strongest, $\text{N}\cdots\text{O} = 2.80$ (1) Å and $\text{N-H}\cdots\text{O} = 175^\circ$.

Experimental

$\text{Au}^{\text{I}}\text{-tu}$ complexes were prepared by stirring together AuHCl_4 (1 mmol) with aqueous tu (x mmol; $1 \leq x \leq 10$) and sulfuric acid (y mmol; $0 \leq y \leq 4$) at room temperature in a 50 ml glass reactor. Freshly prepared base solutions of 0.5 M sulfuric acid and 1 M $(\text{NH}_2)_2\text{CS}$ were prepared from analytical reagent-grade chemicals and MilliQ* water. A 0.1 M AuHCl_4 solution was prepared by dissolving Au in aqua regia, heating to dryness to remove the HNO_3 and dissolving the solid residue with HCl. Complex (I) was obtained by mixing either AuHCl_4 (1 mmol) and aqueous $(\text{NH}_2)_2\text{CS}$ (20 mmol) or AuHCl_4 (1 mmol) and aqueous $(\text{NH}_2)_2\text{CS}$ (3 mmol), *i.e.* no sulfuric acid was present in the base solutions. The amorphous solid obtained on cooling was redissolved in an excess of tu and crystals of (I) subsequently grew at room temperature. Complex (II) was obtained by mixing either AuHCl_4 (1 mmol), $(\text{NH}_2)_2\text{CS}$ (10 mmol) and H_2SO_4

(4 mmol) or AuHCl₄ (1 mmol), (NH₂)₂CS (4 mmol) and H₂SO₄ (2 mmol). The brown precipitate which formed was redissolved by adding an excess of tu, and crystals of (II) were grown at room temperature. In all cases, the crystals were dried in air.

Compound (I)

Crystal data

[Au(CH₄N₂S)₂]Cl
M_r = 384.66
 Monoclinic, *C*2/*c*
a = 8.3991 (10) Å
b = 15.510 (3) Å
c = 7.1584 (10) Å
 β = 104.261 (10)°
V = 903.8 (2) Å³
Z = 4

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
*T*_{min} = 0.703, *T*_{max} = 0.999
 1456 measured reflections
 1313 independent reflections
 837 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.031
wR (*F*²) = 0.102
S = 1.07
 1313 reflections
 49 parameters
 H-atom parameters constrained

D_x = 2.827 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 23 reflections
 θ = 8.4–20.7°
 μ = 16.97 mm⁻¹
T = 293 (2) K
 Cut fragment, colourless
 0.25 × 0.22 × 0.20 mm
*R*_{int} = 0.026
 θ_{\max} = 30°
h = -11 → 11
k = 0 → 21
l = 0 → 10
 2 standard reflections
 frequency: 30 min
 intensity decay: 2%
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 2.2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.19 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.28 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0086 (6)

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1A...Cl ⁱ	0.86	2.41	3.200 (7)	152
N1–H1B...Cl ⁱⁱ	0.86	2.87	3.489 (6)	131
N2–H2A...Cl ⁱ	0.86	2.77	3.480 (7)	141
N2–H2A...S ⁱⁱⁱ	0.86	2.99	3.548 (6)	125
N2–H2B...Cl	0.86	2.70	3.429 (7)	143
N2–H2B...S ^{iv}	0.86	3.01	3.536 (6)	121

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

Compound (II)

Crystal data

[Au(CH₄N₂S)₂]₂SO₄
M_r = 794.48
 Triclinic, *P*1̄
a = 8.0590 (1) Å
b = 11.4980 (2) Å
c = 20.0690 (4) Å
 α = 88.8130 (9)°
 β = 85.0540 (11)°
 γ = 88.2170 (12)°
V = 1851.52 (5) Å³
Z = 4
D_x = 2.850 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 866 reflections
 θ = 3.1–27.4°
 μ = 16.42 mm⁻¹
T = 293 (2) K
 Plate, colourless
 0.38 × 0.37 × 0.14 mm

Table 2

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N11–H11A...O12	0.86	2.25	3.021 (12)	149
N11–H11B...O23	0.86	2.12	2.889 (12)	148
N13–H13A...O12	0.86	2.21	2.990 (13)	150
N13–H13B...S21 ⁱ	0.86	2.86	3.651 (10)	154
N12–H12A...O13 ⁱⁱ	0.86	2.03	2.879 (11)	168
N12–H12B...O23	0.86	2.07	2.854 (11)	152
N14–H14A...O12 ⁱⁱ	0.86	2.12	2.969 (13)	172
N21–H21A...O21	0.86	2.00	2.850 (11)	172
N21–H21B...O14	0.86	2.16	2.920 (11)	147
N23–H23A...O24	0.86	2.09	2.935 (12)	169
N22–H22A...O24 ⁱⁱⁱ	0.86	2.24	2.997 (11)	147
N22–H22A...S41	0.86	2.93	3.473 (9)	123
N22–H22B...O14	0.86	2.18	2.923 (11)	145
N24–H24A...O24 ⁱⁱⁱ	0.86	2.20	2.965 (13)	148
N24–H24B...S12 ^{iv}	0.86	2.82	3.633 (10)	159
N31–H31A...O11 ^v	0.86	2.02	2.863 (13)	166
N31–H31B...S42 ^{vi}	0.86	3.02	3.643 (11)	131
N33–H33A...O13 ^v	0.86	2.15	2.926 (13)	149
N33–H33A...S41 ^v	0.86	2.94	3.369 (9)	112
N33–H33B...O22 ^{vii}	0.86	2.54	2.949 (11)	110
N32–H32A...O11	0.86	2.17	2.942 (12)	149
N32–H32A...O14	0.86	2.49	3.179 (13)	138
N32–H32B...N44 ^v	0.86	2.63	3.198 (13)	125
N34–H34A...O14	0.86	2.48	3.167 (13)	137
N34–H34B...O12 ^{viii}	0.86	2.10	2.950 (13)	171
N41–H41A...O22 ^{ix}	0.86	2.06	2.896 (12)	163
N43–H43A...O23 ^{ix}	0.86	2.31	3.061 (13)	146
N43–H43B...O24 ⁱⁱⁱ	0.86	2.24	3.093 (13)	173
N42–H42A...O22 ^v	0.86	2.01	2.866 (13)	174
N44–H44A...O21 ^v	0.86	1.94	2.799 (12)	175
N44–H44B...O11 ^v	0.86	2.20	2.901 (11)	139

Symmetry codes: (i) 1 - *x*, 1 - *y*, -*z*; (ii) *x*, *y* - 1, *z*; (iii) *x*, 1 + *y*, *z*; (iv) 2 - *x*, 1 - *y*, -*z*; (v) 1 - *x*, 1 - *y*, 1 - *z*; (vi) -*x*, 1 - *y*, 1 - *z*; (vii) 1 - *x*, -*y*, 1 - *z*; (viii) *x* - 1, *y*, *z*; (ix) *x* - 1, 1 + *y*, *z*.

Data collection

Nonius KappaCCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: Gaussian
 integration (Coppens, 1970)
*T*_{min} = 0.010, *T*_{max} = 0.131
 18 534 measured reflections

8386 independent reflections
 7569 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.067
 θ_{\max} = 27.4°
h = -10 → 10
k = -14 → 14
l = -25 → 25

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.049
wR (*F*²) = 0.139
S = 1.08
 8386 reflections
 415 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 22.72P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.49 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -3.03 \text{ e } \text{Å}^{-3}$

A numerical absorption correction could not be applied to the first structure because of the irregular shape of the crystal, a fragment cut from a larger sample. Therefore, an absorption correction based on ψ scans was applied. For (I), the eight H atoms were detected among the first 13 peaks of a difference Fourier map, lying close to the SCN₂ plane, as expected. The H atoms were therefore positioned stereochemically on the corresponding tu plane and refined using a riding model, with N–H constrained to 0.86 Å and *U*_{iso}(H) = 1.2*U*_{eq}(N). For (II), 11 H atoms were detected among the first 30 peaks of a difference Fourier map. The H atoms were positioned and refined as described for (I).

For compound (I), data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995). For compound (II), data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*. For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1485). Services for accessing these data are described at the back of the journal.

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