

3157 reflections  
169 parameters  
H atoms constrained  
 $w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Suenaga, Y., Maekawa, M., Kuroda-Sowa, T., Munakata, M., Morimoto, H., Hiyama, N. & Kitagawa, S. (1997). *Anal. Sci.* **13**, 1047–1049.  
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Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ag1—S1	2.521 (2)	O1—C2	1.21 (1)
Ag1—S2	2.601 (2)	O2—C4	1.20 (1)
S1—C1	1.769 (7)	O6—C11	1.23 (2)
S1—C5	1.83 (1)	C1—C2	1.512 (9)
S2—C3	1.750 (7)	C1—C3'	1.347 (10)
S2—C8	1.854 (10)	C3—C4	1.494 (9)
S1—Ag1—S1'	151.5 (1)	Ag1—S1—C1	103.1 (3)
S1—Ag1—S2	118.22 (8)	Ag1—S1—C5	114.1 (3)
S1—Ag1—S2'	81.25 (7)	Ag1—S2—C3	102.2 (2)
S2—Ag1—S2'	98.8 (1)	Ag1—S2—C8	110.0 (3)

Symmetry code: (i)  $x, \frac{1}{2} - y, 1 - z$ .

Data collection: *Rigaku/AFC Diffractometer Control* (Rigaku Corporation, 1991). Cell refinement: *Rigaku/AFC Diffractometer Control*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1009). Services for accessing these data are described at the back of the journal.

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## Bis(imidazolidine-2-thione)gold(I) diiodaurate(I)

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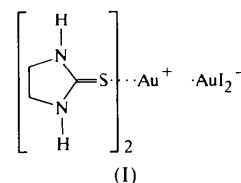
(Received 24 May 1999; accepted 15 June 1999)

## Abstract

The title compound,  $[\text{Au}(\text{C}_3\text{H}_6\text{N}_2\text{S}_2)]_2[\text{AuI}_2]$ , is ionic rather than molecular. The Au atoms of both ions lie on inversion centres. The ions are linked to form linear chains by Au...Au contacts. Two weak N—H...I hydrogen bonds are observed: one is formed within the chain and one links adjacent chains.

## Comment

Imidazoline-2-thione (ethylenethiourea, etu) has been known as a ligand in gold(I) complexes since the work of Morgan & Burstall (1928). Amongst other compounds, they reported  $[(\text{etu})_2\text{Au}]\text{Cl}\cdot\text{H}_2\text{O}$ , the structure of which was determined, and then recently redetermined with higher precision by us (Jones *et al.*, 1976; Jones & Friedrichs, 1999a);  $[(\text{etu})\text{Au}]_2\text{O}$ , which we have recently shown to be a tetramer of gold(I) with deprotonated etu (Jones & Friedrichs, 1999b); and  $(\text{etu})\text{AuI}$ , (I), the structure of which we report here.



The asymmetric unit of the title compound is shown in Fig. 1. It is in fact ionic, having the form  $[(\text{etu})_2\text{Au}]^+[\text{AuI}_2]^-$ , rather than being the molecular  $(\text{etu})\text{AuI}$ . Both Au atoms lie on inversion centres and thus exhibit ideal linear coordination geometry, with

Au—S = 2.318 (2) and Au—I = 2.5558 (6) Å. A search of the Cambridge Structural Database (Version of October 1998; Allen & Kennard, 1993) yielded eight hits for comparable bis(thione)gold(I) cations, with an average Au—S bond length of 2.289 Å {*c.f.* our values of 2.2852 and 2.2881 (12) Å in [(*etu*)<sub>2</sub>Au]Cl·H<sub>2</sub>O; Jones & Friedrichs, 1999*a*}. A similar search for the AuI<sub>2</sub><sup>-</sup> anion gave 13 hits, with a mean Au—I distance of 2.564 Å.

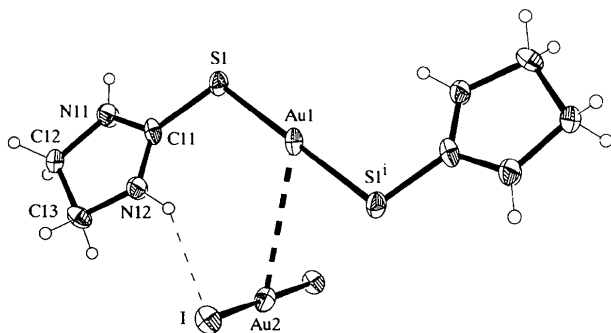


Fig. 1. The structure of (I) in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. One hydrogen bond and one Au...Au contact are shown (see text) [symmetry code: (i)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ].

The Au atoms are linked into infinite chains (exactly linear by symmetry) parallel to the *x* axis by short Au1...Au2 contacts of 3.2701 (6) Å (Fig. 2). The alternating anions and cations are staggered with respect to each other, with an S1—Au1...Au2—I torsion angle of  $-106.03(6)^\circ$ . A similar chain was observed for [(*tht*)<sub>2</sub>Au]<sup>+</sup>[AuI<sub>2</sub>]<sup>-</sup> [*tht* is tetrahydrothiophene; Au...Au 2.967 (2) and 2.980 (2) Å, and torsion angles 155.46 (4) and 161.25 (4) $^\circ$ ; Ahrlund *et al.*, 1985].

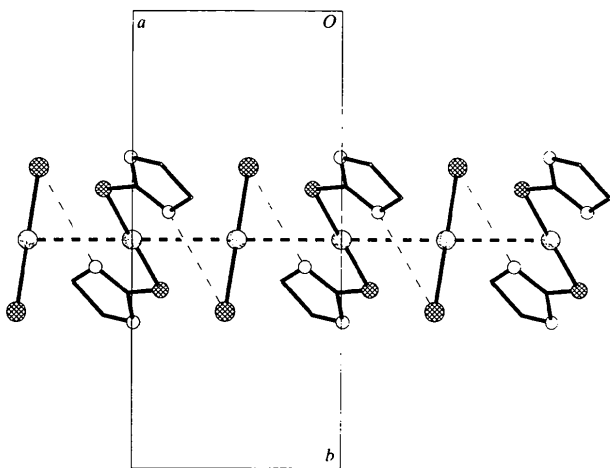


Fig. 2. Part of the anion-cation chain. H atoms have been omitted for clarity. Atomic radii are arbitrary.

In [(*py*)<sub>2</sub>Au]<sup>+</sup>[AuI<sub>2</sub>]<sup>-</sup> (*py* is pyridine; Adams *et al.*, 1982), tetranuclear assemblies of the type anion-cation-cation-anion form a linear Au<sub>4</sub> chain with Au...Au distances of 2.990 (1) and 3.291 (1) Å.

The two N—H groups are classical hydrogen-bond donors; the only possible acceptors are the I atoms. Consequently, two weak hydrogen bonds are formed: N12—H12...I lies within the asymmetric unit (Fig. 1), whereas N11—H11...I connects neighbouring chains of ions (Table 3). The H...I distances of 3.08 (6) and 3.05 (6) Å can be corrected to 2.97 and 2.95 Å, respectively, assuming normalized N—H bond lengths of 1.009 Å, but they are still appreciably greater than the value of *ca* 2.7 Å for various N—H...I<sup>-</sup> systems quoted in a database analysis by Steiner (1998).

## Experimental

The title compound was prepared as described by Morgan & Burstall (1928) from [(*etu*)<sub>2</sub>Au]Cl and potassium iodide in water and recrystallized from an ethanol/acetonitrile solution by diffusion of diethyl ether.

### Crystal data

[Au(C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>S)<sub>2</sub>][AuI<sub>2</sub>]

*M<sub>r</sub>* = 852.05

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 6.5401 (12) Å

*b* = 14.0889 (18) Å

*c* = 8.1843 (12) Å

$\beta$  = 99.753 (12) $^\circ$

*V* = 743.2 (2) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 3.807 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo K $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 69 reflections

$\theta$  = 2.9–12.5 $^\circ$

$\mu$  = 24.13 mm<sup>-1</sup>

*T* = 173 (2) K

Tapered prism

0.30 × 0.10 × 0.05 mm

Colourless

### Data collection

Siemens P4 diffractometer

$\omega$  scans

Absorption correction:

$\psi$  scan (XEMP; Siemens, 1994*a*)

*T<sub>min</sub>* = 0.123, *T<sub>max</sub>* = 0.299

2791 measured reflections

1310 independent reflections

982 reflections with

*I* > 2 $\sigma$ (*I*)

*R<sub>int</sub>* = 0.035

$\theta_{\max}$  = 25 $^\circ$

*h* = 0 → 7

*k* = -16 → 16

*l* = -9 → 9

3 standard reflections

every 247 reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

$R[F^2 > 2\sigma(F^2)] = 0.024$

*wR*(*F*<sup>2</sup>) = 0.050

*S* = 0.914

1310 reflections

84 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

( $\Delta/\sigma$ )<sub>max</sub> < 0.001

$\Delta\rho_{\max} = 0.78 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.24 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a'_i a'_j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
Au1	0	1/2	1/2	0.02106 (13)
S1	-0.1380 (4)	0.61139 (13)	0.3035 (3)	0.0203 (4)
C11	0.0191 (13)	0.6174 (5)	0.1586 (10)	0.0195 (17)
N11	-0.0072 (12)	0.6813 (5)	0.0372 (9)	0.0266 (17)
C12	0.1373 (12)	0.6658 (6)	-0.0807 (9)	0.0235 (17)
C13	0.2829 (12)	0.5919 (6)	0.0079 (11)	0.0228 (18)
N12	0.1742 (11)	0.5606 (5)	0.1414 (9)	0.0250 (16)
Au2	1/2	1/2	1/2	0.02429 (13)
I	0.44663 (9)	0.34110 (4)	0.34810 (7)	0.02635 (14)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Au1—S1	2.318 (2)	S1—C11	1.698 (8)
Au1—Au2	3.2701 (6)	Au2—I	2.5558 (6)
S1—Au1—S1'	180	I—Au2—I <sup>iii</sup>	180
S1—Au1—Au2	105.78 (6)	I—Au2—Au1	86.895 (5)
Au2—Au1—Au2 <sup>ii</sup>	180	Au1—Au2—Au1 <sup>iv</sup>	180
C11—S1—Au1	107.9 (3)		

Symmetry codes: (i)  $-x, 1-y, 1-z$ ; (ii)  $x-1, y, z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $1+x, y, z$ .

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...I'	0.89 (5)	3.08 (6)	3.889 (7)	153 (6)
N12—H12...I	0.88 (5)	3.05 (6)	3.818 (7)	147 (7)

Symmetry code: (i)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

H atoms bonded to nitrogen were located from Fourier syntheses and refined freely, but with the N—H distances restrained to be equal using a *SADI* instruction (Sheldrick, 1997). Other H atoms were placed in calculated positions and refined using a riding model.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994b). 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: BM1346). Services for accessing these data are described at the back of the journal.

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## Complexation of $\omega$ -thiocaprolactam with heavy metals: terminal and bridging coordination modes in cadmium and silver compounds

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## Abstract

The soft base  $\omega$ -thiocaprolactam (1-azacycloheptane-2-thione, Hthcl) reacts with  $\text{Cd}^{\text{II}}$  and  $\text{Ag}^{\text{I}}$  nitrate salts, giving two new coordination complexes,  $[\text{Cd}(\text{NO}_3)_2(\text{C}_6\text{H}_{11}\text{NS})_4]$  and  $[\text{Ag}_4(\text{C}_6\text{H}_{11}\text{NS})_8](\text{NO}_3)_4$ . The first compound, tetrakis(1-azacycloheptane-2-thione-*S*)bis(nitrate-*O*)cadmium(II), presents a slightly distorted octahedral coordination geometry, with two  $\eta^1$ - $\text{NO}_3$  fragments in a *cis* arrangement and four Hthcl molecules bonded *via* the S atom of the thiocarbonyl group; coordination bond lengths involving S atoms range from 2.5768 (19) to 2.6828 (18) Å. The cationic moiety of the silver compound, tetrakis[ $\mu$ -(1-azacycloheptane-2-thione-*S*)]tetrakis[(1-azacycloheptane-2-thione-*S*)silver(I)] tetranitrate, is a centrosymmetric tetranuclear cluster containing eight Hthcl molecules, four of which are in terminal positions [coordination distances 2.4850 (19) and 2.478 (2) Å], as in the Cd complex, while the other four bridge two metallic ions each, with coordination distances in the range 2.4608 (17)–2.6976 (18) Å.

## Comment

Solvent extraction is one of the most important methods for the isolation and separation of metal ions. It is well