

# 1,2-Dicyano-1,2-bis(imidazolidine-2-thione)digold(I) and 2,2-dicyano-1,1-bis(dimethylthiourea)digold(I)

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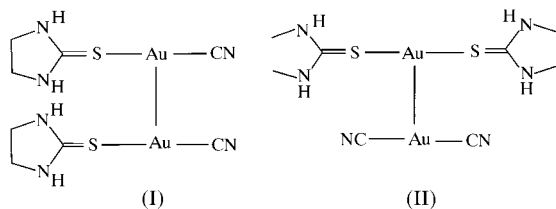
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Gold(I) cyanide forms complexes with imidazolidine-2-thione (etu) and dimethylthiourea (dmu) with the formula  $[\text{Au}_2(\text{CN})_2\text{L}_2]$ , *i.e.* the title complexes dicyano-1 $\kappa$ C,2 $\kappa$ C-bis-(imidazolidine-2-thione)-1 $\kappa$ S,2 $\kappa$ S-digold(I)(Au—Au),  $[\text{Au}_2(\text{CN})_2(\text{C}_3\text{H}_6\text{N}_2\text{S})_2]$ , and dicyano-1 $\kappa^2$ C-bis(*N,N'*-dimethylthiourea)-2 $\kappa^2$ S-digold(I)(Au—Au),  $[\text{Au}_2(\text{CN})_2(\text{C}_3\text{H}_8\text{N}_2\text{S})_2]$ . In the etu complex, two approximately linear (etu)AuCN groups are held together by a weak homopolar Au—Au bond [3.117 (1) Å], with a torsion angle of 61 (3)° between the two groups. In the dmtu complex, an approximately linear Au(dmtu)<sub>2</sub> group is bound to an approximately linear Au(CN)<sub>2</sub> group by a weak heteropolar Au—Au bond [3.091 (1) Å], with a torsion angle of 83 (5)° between the two groups.

## Comment

We have reported previously the preparation and structures of complexes of thioureas with copper(I) cyanide (Stocker *et al.*, 1996) and with silver(I) cyanide (Stocker *et al.*, 2000). We report here an extension of this work to gold(I) cyanide. The sulfur ligands used previously included thiourea (tu), 1-methyl-2-thiourea (mtu), 1,3-dimethyl-2-thiourea, 1,3-diethyl-2-thiourea (detu), 1,1,3,3-tetramethylthiourea (tmtu) and 2-imidazolidinethione (*N,N*-ethylenethiourea, etu). For the



purposes of comparison, syntheses were attempted of the gold cyanide complexes of all of these ligands. Crystalline products could only be obtained with dmtu and etu, and the structures of 1,2-dicyano-1,2-bis(imidazolidine-2-thione)digold(I), (I),

and 2,2-dicyano-1,1-bis(dimethylthiourea)digold(I), (II), are reported here.

Ellipsoid plots indicating the atom labeling are shown in Figs. 1 and 2 for (I) and (II), respectively. In each case, there is a molecule containing two Au atoms, two CN groups and two thioureas, and the molecule is shaped like a twisted letter H with two approximately linear AuX<sub>2</sub> or AuXY groups held together by a weak Au—Au bond. Because the end groups are not exactly linear, the torsion angles around the Au—Au bond are not well defined. An average torsion angle can be obtained from the four individual torsion angles involving the Au—Au bond; this is 61 (3)° for the etu complex and 83 (5)° for the dmtu complex.

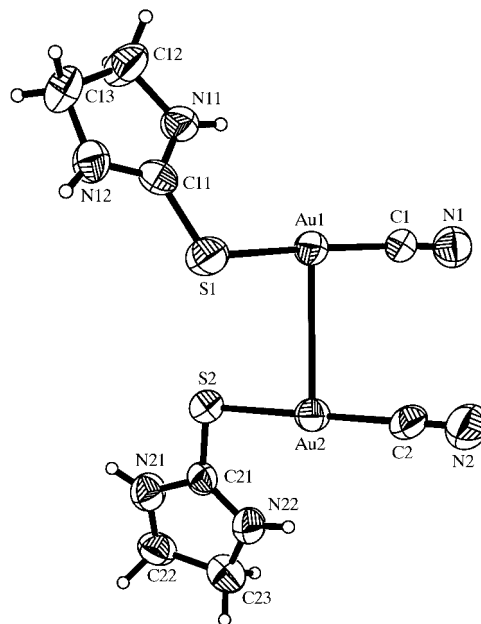


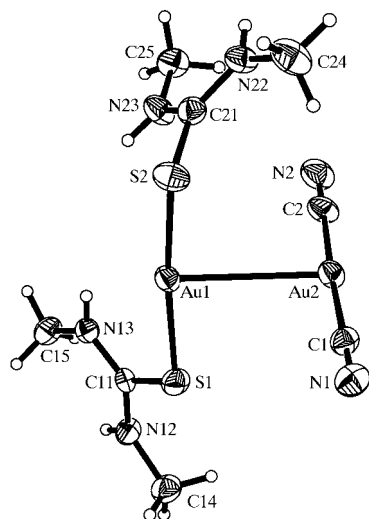
Figure 1

Plot of the etu complex with displacement ellipsoids shown at the 50% probability level. H atoms are shown as circles of arbitrary size.

The two molecules differ, however, in that the etu complex contains two (etu)AuCN groups, while in the dmtu complex, there is one Au(dmtu)<sub>2</sub> group and one Au(CN)<sub>2</sub> group. It is somewhat surprising that such a minor chemical change in the ligand in going from etu to dmtu should lead to a change in the isomer of  $[\text{Au}_2(\text{CN})_2\text{L}_2]$  that is formed. Although the two compounds appear to be quite different in that the Au—Au bond in the etu complex is non-polar while that in the dmtu complex is polar, the occurrence of the two forms suggests that they differ very little in energy.

Every H atom attached to nitrogen in both structures is involved in hydrogen bonding (Tables 2 and 4).

Gold compounds of this sort are well known. Bis[iodo(trimethylphosphine)gold(I)] (Ahrland *et al.*, 1987) is an example of a non-polar Au—Au complex (Au—Au 3.169 Å and torsion angle 70°), bis(imidazolidene-2-thione)gold(I) diiodoaurate (Friedrichs & Jones, 1999) is an example of a polar isomer with etu as a ligand (3.270 Å and 74°) and dicyanobis[tris(2-cyanoethyl)phosphine]digold (Hussain *et al.*, 1996) is an example containing the Au(CN)<sub>2</sub> group (3.270 Å and 80°).



**Figure 2**  
Plot of the dtmu complex with displacement ellipsoids shown at the 50% probability level. H atoms are shown as circles of arbitrary size.

It is worth noting that the etu complex could be planar and have a center of symmetry; the sizes of the C and S atoms do not preclude such an arrangement. While it is possible that packing forces account for the lack of a center, none of the 13 Au<sub>2</sub> complexes in the current version of the Cambridge Structural Database (Allen & Kennard, 1993) has a torsion angle around the Au—Au bond of less than 60°. This suggests that perhaps a torsion angle near 90° is favored energetically in the isolated molecule.

In both of the complexes reported here, there are Au—Au bonds, terminal CN groups and discrete molecules. This is different from the situation when the metal is Cu or Ag. In the seven complexes of CuCN with various thioureas (Stocker *et al.*, 1996), there are 14 crystallographically different CN groups, 13 of which bridge between two Cu atoms. There are no Cu—Cu bonds. In the six complexes of AgCN with various thioureas (Stocker *et al.*, 2000), there are nine crystallographically different CN groups, five of which bridge between two Ag atoms, and one of which is involved in what appears to be a three-center bond with two Ag atoms. The latter is the only example of a direct Ag—Ag interaction in any of the six complexes. About half of the time in both the Cu and Ag complexes, the S atom bridges between the metal atoms. As a consequence of the CN and S bridges, all of the Cu and Ag complexes have polymeric solid-state structures. In the two examples presented here, the direct Au—Au bonds, which have no parallel in the Cu or Ag structures, lead to a completely different structural chemistry.

## Experimental

Commercial chemicals were used without further purification. For the preparation of AuCN(etu), (I), AuCN (56 mg, 0.25 mmol) was added to a solution of etu (177 mg, 1.67 mmol) in distilled water (10 ml). After heating to 363 K, a colorless solution was obtained which was

filtered hot. Upon cooling, colorless crystals separated out (yield: 47 mg, 69%). IR (KBr): 3460 (*m*), 3220 (*br s*), 3070 (*w*), 2890 (*m*), 2155 (*s*), 1540 (*s*), 1482 (*w*), 1375 (*m*), 1320 (*m*), 1285 (*s*), 1212 (*m*), 1043 (*w*), 1015 (*w*), 997 (*w*), 917 (*m*), 750 (*br m*), 660 (*w*), 585 (*br m*), 495 (*w*), 445 (*m*) cm<sup>-1</sup>. Analysis calculated for C<sub>4</sub>H<sub>6</sub>AuN<sub>3</sub>S: C 14.78, H 1.86, N 12.92, S 9.86%; found: C 14.94, H 1.59, N 13.01, S 9.73%. For the preparation of AuCN(dmtu), (II), AuCN (56 mg, 0.25 mmol) was added to a solution of dmtu (661 mg, 5.0 mmol) dissolved in distilled water (10 ml). Mild heating (343 K) for about 30 min produced a clear colorless solution. Upon cooling, small block-like colorless crystals were deposited (yield: 60 mg, 73%). IR (KBr): 3385 (*m*), 3290 (*s*), 3235 (*sh w*), 3175 (*w*), 2960 (*w*), 2150 (*s*), 1617 (*m*), 1595 (*s*), 1530 (*m*), 1505 (*s*), 1455 (*m*), 1422 (*m*), 1375 (*w*), 1290 (*s*), 1190 (*m*), 1148 (*w*), 1042 (*m*), 1015 (*w*), 725 (*m*), 630 (*w*), 605 (*w*), 510 (*m*), 428 (*w*) cm<sup>-1</sup>. Analysis calculated for C<sub>4</sub>H<sub>8</sub>AuN<sub>3</sub>S: C 14.69, H 2.46, N 12.84, S 9.80%; found: C 14.72, H 2.57, N 12.86, S 9.76%.

## Compound (I)

### Crystal data

[Au<sub>2</sub>(CN)<sub>2</sub>(C<sub>3</sub>H<sub>6</sub>N<sub>2</sub>S)<sub>2</sub>]  
M<sub>r</sub> = 650.28  
Triclinic, P $\bar{1}$   
a = 7.4654 (15) Å  
b = 9.233 (2) Å  
c = 11.895 (2) Å  
α = 103.73 (3)°  
β = 90.73 (3)°  
γ = 112.98 (3)°  
V = 728.1 (3) Å<sup>3</sup>

Z = 2  
D<sub>x</sub> = 2.966 Mg m<sup>-3</sup>  
Mo Kα radiation  
Cell parameters from 1873 reflections  
θ = 1.8–25.0°  
μ = 20.403 mm<sup>-1</sup>  
T = 174 (2) K  
Flat needle, colorless  
0.30 × 0.10 × 0.06 mm

### Data collection

Siemens SMART area-detector diffractometer  
ω scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)  
T<sub>min</sub> = 0.10, T<sub>max</sub> = 0.29  
5410 measured reflections  
2545 independent reflections  
2124 reflections with I > 2σ(I)

R<sub>int</sub> = 0.045  
θ<sub>max</sub> = 25.03°  
h = -8 → 8  
k = -10 → 10  
l = -14 → 14  
93 standard reflections  
frequency: the first 93 reflections were remeasured at the end of the data collection 10 h later  
intensity decay: <1%

**Table 1**

Selected geometric parameters (Å, °) for (I).

Au1—Au2	3.1167 (10)	Au1—C1	1.964 (10)
Au1—S1	2.292 (3)	Au2—C2	1.968 (10)
Au2—S2	2.295 (3)		
C1—Au1—S1	173.6 (3)	C2—Au2—S2	179.6 (3)
C1—Au1—Au2—C2	57.8 (4)	C1—Au1—Au2—S2	-122.5 (3)
S1—Au1—Au2—C2	-116.2 (3)	S1—Au1—Au2—S2	63.42 (10)

**Table 2**

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

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...S2 <sup>i</sup>	0.86	2.76	3.556 (8)	155
N12—H12...N1 <sup>ii</sup>	0.86	2.14	2.999 (12)	172
N21—H21...N1 <sup>iii</sup>	0.86	2.15	2.988 (12)	163
N22—H22...N2 <sup>iv</sup>	0.86	2.07	2.880 (13)	157

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

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.093$   
 $S = 0.94$   
 2545 reflections  
 163 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0650P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.005$   
 $\Delta\rho_{\max} = 1.91 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.52 \text{ e } \text{\AA}^{-3}$

## Compound (II)

### Crystal data

$[\text{Au}_2(\text{CN})_2(\text{C}_3\text{H}_8\text{N}_2\text{S})_2]$   
 $M_r = 654.32$   
 Monoclinic,  $P2_1/c$   
 $a = 13.3922(2) \text{ \AA}$   
 $b = 7.81700(10) \text{ \AA}$   
 $c = 14.9588(3) \text{ \AA}$   
 $\beta = 94.5060(10)^\circ$   
 $V = 1561.15(4) \text{ \AA}^3$   
 $Z = 4$

$D_x = 2.784 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 2105 reflections  
 $\theta = 1.5\text{--}25.0^\circ$   
 $\mu = 19.033 \text{ mm}^{-1}$   
 $T = 174(2) \text{ K}$   
 Needle, colorless  
 $0.16 \times 0.06 \times 0.04 \text{ mm}$

### Data collection

Siemens SMART area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996; Blessing, 1995)  
 $T_{\min} = 0.27$ ,  $T_{\max} = 0.47$   
 7629 measured reflections  
 2737 independent reflections  
 2421 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$   
 $\theta_{\max} = 25.03^\circ$   
 $h = -14 \rightarrow 15$   
 $k = -9 \rightarrow 8$   
 $l = -17 \rightarrow 17$   
 108 standard reflections  
 frequency: the first 108 reflections were remeasured at the end of the data collection 14 h later  
 intensity decay:  $<1\%$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.063$   
 $S = 1.07$   
 2737 reflections  
 168 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 1.97 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.27 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: SHELXTL  
 Extinction coefficient:  
 $3.5(8) \times 10^{-4}$

**Table 3**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

Au1—Au2	3.0911 (4)	Au2—C1	1.983 (8)
Au1—S1	2.285 (2)	Au2—C2	1.984 (8)
Au1—S2	2.304 (2)		
S1—Au1—S2	169.70 (7)	C1—Au2—C2	176.7 (3)
S1—Au1—Au2—C1	−79.5 (2)	S1—Au1—Au2—C2	102.9 (2)
S2—Au1—Au2—C1	91.8 (2)	S2—Au1—Au2—C2	−85.7 (2)

**Table 4**

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N12—H12 $\cdots$ N2 <sup>i</sup>	0.86	2.55	3.207 (8)	134
N13—H13 $\cdots$ N1 <sup>ii</sup>	0.86	2.23	2.972 (9)	144
N22—H22 $\cdots$ N2 <sup>iii</sup>	0.86	2.13	2.936 (10)	156
N23—H23 $\cdots$ N1 <sup>ii</sup>	0.86	2.15	2.968 (8)	158

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

In the final difference map for the etu compound there are 21 peaks and valleys with magnitudes greater than  $0.75 \text{ e } \text{\AA}^{-3}$ ; for the dtmu compound there are 15 such peaks. In both cases, all of these are between 0.85 and  $1.20 \text{ \AA}$  from one or other of the Au atoms.

For both compounds, data collection: ASTRO (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1994); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1525). Services for accessing these data are described at the back of the journal.

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