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Monoammonium Bis(D-penicillaminato-*S*)-aurate(I) 3.667-Hydrate

Daren J. LeBlanc, James F. Britten, Zhixian Wang, Helen E. Howard-Lock and Colin J. L. Lock†

Department of Chemistry, McMaster University, Hamilton, ON, Canada L8S 4M1. E-mail: leblancd@mcmaster.ca

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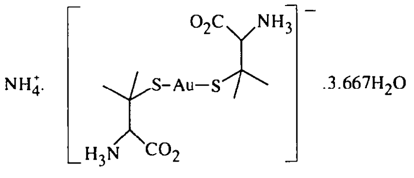
Abstract

The anion of the title compound, $(NH_4)[Au(C_5H_{10}NO_2S)_2].3.667H_2O$, has roughly linear coordination of the Au atom to the S atoms of the ligands [Au—S 2.2900 (13) Å and S—Au—S 178.47 (7)°]. The C—S···S—C torsion angle is 29.3 (2)°. The packing arrangement is determined by short Au···Au contacts [3.221 (1) Å] as well as hydrogen-bonding interactions between ligand carboxylate and amine functional groups, the ammonium counter-cation and water molecules of hydration. Bond lengths and angles are normal.

Comment

The gold-based anti-arthritis drug myochrysine (gold sodium thiomalate) has been shown to be a mixture of at least five components (Harvey, Howard-Lock & Lock, 1988). Despite the use of this drug for more than fifty years, the structure of the gold-containing components is unknown. Although the main gold-containing component is believed to be polymeric, the size and structure of the polymer has yet to be determined. During the course of investigations into the preparation and characterization of gold-drug model complexes, several 1:2 gold:thiol-ligand complexes have been isolated. Although these complexes are not likely to be directly analogous to the main component of the drug mixture, they are the simplest possible gold-drug model compounds and have potential as anti-arthritic agents. The structure of such a D-penicillamine–gold complex, (I), is reported here. The preparation and characterization of several analogous gold–thiomalate complexes have been reported elsewhere (LeBlanc, Smith, Wang, Howard-Lock & Lock, 1997).



(I)

The molecular anion is shown in Fig. 1. The ligating S atoms form the expected nearly linear arrangement around the Au atom [S—Au—S 178.47 (7)°] and the Au—S bond length [2.2900 (13) Å] is in the normal range for monomeric complexes of this type (Usón *et al.*, 1990; Bates & Waters, 1985; Jones, Guy & Sheldrick, 1976; Ruben, Zalkin, Faltens & Templeton, 1974). All other bond lengths and angles are normal. The C—S···S—C torsion angle is 29.3 (2)°. The analogous torsion angle in other complexes of this type ranges from 20.8 (Jones, Guy & Sheldrick, 1976) to 180° (Usón *et al.*, 1990). If $d\pi$–$d\pi$ bonding was present, as has been suggested for complexes of this type (Bates & Waters, 1985; Drew & Riedl, 1973), the extent of this interaction would be maximized if one S atom was involved in $d_{xz}\pi$–$d_{xz}\pi$ bonding and the other was involved in $d_{yz}\pi$–$d_{yz}\pi$ bonding, when the C—S—Au planes should be roughly at right angles to each other. The extent of this multiple bonding must be small, however, considering the large variations from 90° observed for the torsion angles for this type of complex. It appears that packing forces are the dominant factor in determining the C—S···S—C torsion angle.

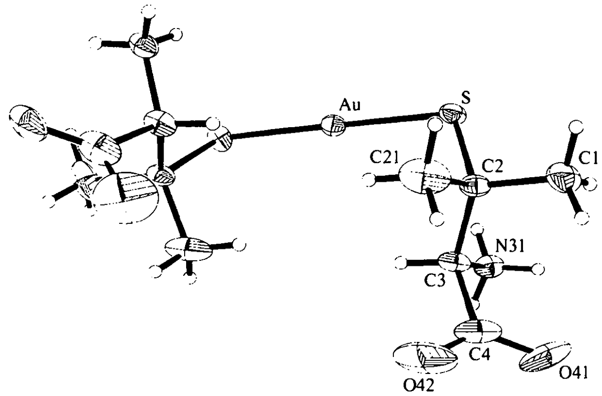


Fig. 1. The title anion drawn with 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

A packing diagram for the title complex is shown in Fig. 2. The S—Au—S cores, arranged around the origin (a threefold axis), are in relatively close contact, with Au···Au distances of 3.221 (1) Å. This distance is within the range of Au···Au aurophilic interactions, an attractive force which has been attributed to relativistic effects (Li & Pyykkö, 1992; Pyykkö & Zhao, 1991) and has been shown to be of similar magnitude to hydrogen bonding (Schmidbaur, Graf & Müller, 1988; Schmidbaur, Dziwok, Grohmann & Müller, 1989).

There is an extensive hydrogen-bonding network throughout the crystal of this complex. The amine functional groups of the ligand form hydrogen bonds to carboxylate functional groups on neighbouring ligands [N···O 2.703 (6) and 2.740 (7) Å]. The ammonium

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† Deceased.

counter-cations also form hydrogen bonds to the ligand carboxylates [N···O 2.835 (5) and 3.146 (13) Å]. The water molecules of hydration are involved in hydrogen bonding to ligand amine functional groups [N···O 2.929 (7) Å], ligand carboxylates [O···O 2.782 (7) and 2.988 (8) Å] and other waters of hydration [O···O 2.868 (5), 2.877 (8) and 2.955 (7) Å].

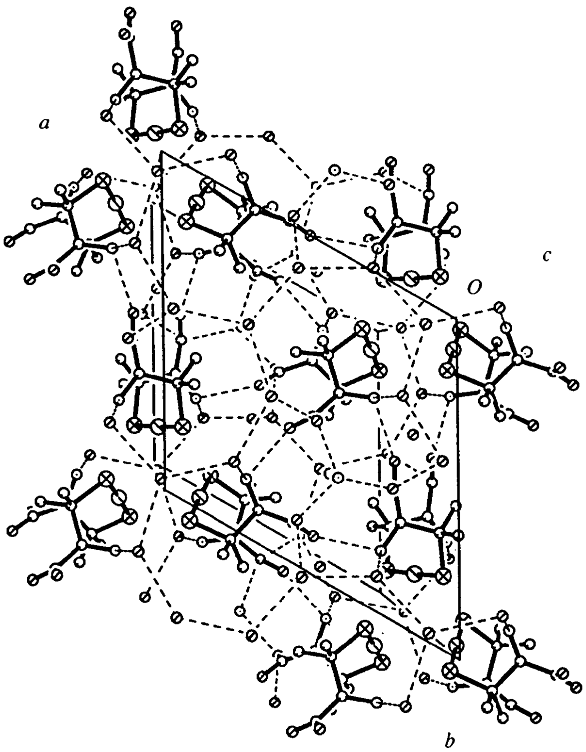

Fig. 2. Packing of the title compound in the unit cell. Hydrogen bonds are indicated by broken lines.

Experimental

Chloro(tetrahydrothiophene)gold(I) (200 mg, 0.62 mmol) was added, with continuous stirring and over the course of about 5 min, to a solution of D-penicillamine (200 mg, 1.34 mmol) in 5 ml of methanol. Concentrated ammonium hydroxide was added dropwise to the resultant suspension and a clear colourless solution resulted after the addition of about 1 ml of NH_4OH. Extra NH_4OH was added (1 ml), the solution was gravity filtered into a 10 ml vial which was covered with parafilm, several holes were punched into the parafilm, and the vial was left in a nitrogen atmosphere for 48 h. The resultant colourless crystalline product was collected by filtration; yield 280 mg (78%). Analysis calculated: C 20.8, H 5.5, N 7.3, O 21.2, S 11.1, Au 34.1%; found: C 20.7, H 5.5, N 7.6, S 11.0, Au 34.1%. ^{1}H NMR: δ 1.32, 1.65 (2*s*, 6H, 2 × CH_3), 3.63 (*s*, 1H, CH). ^{13}C NMR: δ 31.2, 38.2 (2 × CH_3), 49.4 [C(S)], 70.0 [C(H)NH_2]. IR/Raman: ν C—S 611, 560, δ CCS 361, δ $(CH_3)_2CS$ 319, ν Au—S 380, δ SAuS 136 cm^{-1}. MS (–ESI): *m/z* (RI%); 378 $[AuLSH_2]^-$ (20), 493 $[AuL_2H_2]^-$ (100), 843 $[Au_2L_3H_3]^-$ (2) (*L* = D-penicillamine dianion).

Crystal data

$(NH_4)[Au(C_5H_{10}NO_2S)_2]$.-$3.667H_2O$
$M_r = 577.47$
Trigonal
$R32$
$a = 11.645\,(2)$ Å
$c = 38.273\,(8)$ Å
$V = 4494.7\,(14)$ Å^3
$Z = 9$
$D_x = 1.920$ Mg m^{-3}
$D_m = 1.91\,(2)$ Mg m^{-3}
D_m measured by flotation in CCl_4/CH_2I_2

Ag $K\alpha$ radiation
$\lambda = 0.56086$ Å
Cell parameters from 23 reflections
$\theta = 7.43$–$14.83°$
$\mu = 4.145$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.40 × 0.25 × 0.08 mm
Colourless

Data collection

Siemens *P*3 diffractometer
ω–2θ scans
Absorption correction: empirical, *via* ψ scans (*SHELXTL*; Sheldrick, 1994)
$T_{min} = 0.371$, $T_{max} = 0.718$
7812 measured reflections
2673 independent reflections

2362 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 22.56°$
$h = -15 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = -52 \rightarrow 52$
3 standard reflections every 97 reflections intensity decay: -2.01%

Refinement

Refinement on F^2
$R = 0.028$
$wR(F^2) = 0.060$
$S = 0.995$
2673 reflections
112 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.93$ e Å^{-3}
$\Delta\rho_{min} = -0.84$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = $-0.01\,(2)$

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Au	0.50700 (2)	1/3	5/6	0.03296 (7)
S	0.45776 (13)	0.24009 (12)	0.77878 (4)	0.0364 (3)
C2	0.3205 (5)	0.2584 (4)	0.7613 (2)	0.0350 (12)
C1	0.2939 (8)	0.1985 (7)	0.7250 (2)	0.067 (2)
C21	0.2003 (5)	0.1874 (6)	0.7843 (2)	0.075 (2)
C3	0.3615 (5)	0.4075 (5)	0.7609 (2)	0.0401 (13)
N31	0.4914 (4)	0.4886 (4)	0.74292 (13)	0.0424 (11)
C4	0.2580 (7)	0.4328 (6)	0.7440 (3)	0.066 (2)
O41	0.2657 (5)	0.4503 (5)	0.7123 (2)	0.083 (2)
O42	0.1703 (6)	0.4277 (8)	0.7642 (2)	0.124 (3)
N1	1/3	2/3	2/3	0.043 (3)
N2	0	0	0.8514 (4)	0.166 (8)
O1	0.0863 (5)	0.2777 (5)	0.66322 (12)	0.0599 (11)
O2	0	0.3700 (9)	0.5000	0.201 (7)
O3†	0	0	0.6662 (7)	0.071 (7)
O4‡	0	0	0.6444 (6)	0.072 (6)

† Site occupancy = 0.46. ‡ Site occupancy = 0.54.

Table 2. *Selected geometric parameters (Å, °)*

Au—S	2.2900 (13)	C3—N31	1.491 (7)
S—C2	1.841 (5)	C3—C4	1.522 (8)
C2—C21	1.502 (8)	C4—O41	1.225 (10)
C2—C1	1.515 (8)	C4—O42	1.257 (10)
C2—C3	1.554 (6)		
S—Au—S^i	178.47 (7)	C3—C2—S	109.5 (3)
C2—S—Au	107.6 (2)	N31—C3—C4	109.4 (5)
C21—C2—C1	111.3 (5)	N31—C3—C2	111.1 (4)
C21—C2—C3	107.6 (5)	C4—C3—C2	112.9 (5)
C1—C2—C3	112.6 (5)	O41—C4—O42	127.3 (7)
C21—C2—S	110.3 (4)	O41—C4—C3	117.0 (7)
C1—C2—S	105.6 (4)	O42—C4—C3	115.6 (8)

Symmetry code: (i) $\frac{1}{3}+x-y, \frac{2}{3}-y, \frac{5}{3}-z$.

Attempts to model O2 as a disordered atom off the special position did not give an improved solution. For the disordered water molecules (O3 and O4) along the 0,0,*z* threefold axis, the isotropic displacement parameters were constrained to be equivalent and the occupancies were allowed to vary, with the constraint that their sum must be no greater than 1. The site occupancies were then fixed and the displacement parameters were allowed to vary. In the final stages, all non-H atoms were refined anisotropically. H atoms were added at calculated positions and allowed to ride on the atoms to which they were attached. Their isotropic displacement parameters (*U*'s) were set to $1.5U_{eq}$ of the atom to which they were attached. H atoms were not added to the ammonium counter-cations or the water molecules of hydration.

Data collection: *P3 Software* (Siemens, 1989). Cell refinement: *P3 Software*. Data reduction: *P3 Software*. 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: FR1038). Services for accessing these data are described at the back of the journal.

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cyclo-Hexakis[(2,4,6-triisopropylthiophenolato-*S*:*S*)gold(I)] Diethyl Ether Solvate

Daren J. LeBlanc and Colin J. L. Lock†

Department of Chemistry, McMaster University, Hamilton, ON, Canada L8S 4M1. E-mail: leblancd@mcmaster.ca

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Abstract

In the title compound, $[Au_6S_6(C_{15}H_{23})_6].C_4H_{10}O$, the gold–thiolate molecule, a centrosymmetric cyclic hexamer with a cyclohexane chair-like structure, lies about an inversion centre. The Au atoms are coordinated in a near-linear fashion to bridging S atoms [Au—S 2.281 (2)–2.288 (3) Å and S—Au—S 173.68 (9)–175.82 (9)°]. Bond lengths and angles are normal.

Comment

The structure of the hexakis[2,4,6-tri(isopropyl)thiophenolatogold(I)] complex has been reported previously as a tetrahydrofuran solvate (Schröter & Strähle, 1991). In an effort to follow up on gold–thiolate mass spectrometry experiments (Howard-Lock, LeBlanc, Lock, Smith & Wang, 1996), it was decided to prepare a sample of Schröter & Strähle's complex and try to obtain a mass spectrum by electrochemical ionization. A slightly different preparation method and a different gold starting material were used as compared to Schröter & Strähle's procedure, but the conditions of crystal growth were similar. An X-ray powder diffraction pattern of the isolated product suggested that the unit cell was different from that observed by Schröter & Strähle (1991) and this was confirmed by determination of the unit cell from a single crystal. It was assumed that a different oligomer had been produced, such as a closed ring tetramer, two of which have recently been reported

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† Deceased.