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catena-Poly[bromo(*ω*-thiocaprolactam-*κS*)gold(I)](*Au*—*Au*)

María-Elena Núñez Gaytán,[a] Sylvain Bernès,[b]* Eduardo Rodríguez de San Miguel[c] and Josefina de Gyves[c]

[a]Facultad de Ingeniería Química, Departamento de Química, Universidad Michoacana de San Nicolás de Hidalgo, Ciudad Universitaria, 58060 Morelia, Mich., Mexico, [b]Centro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, AP 1613, 72000 Puebla, Pue., Mexico, and [c]Departamento de Química Analítica, Facultad de Química, UNAM, Ciudad Universitaria, 04510 México DF, Mexico
Correspondence e-mail: sylvain@eros.pquim.unam.mx

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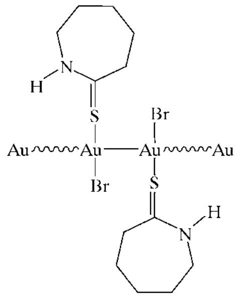
The title compound, $[AuBr(C_6H_{11}NS)]_n$, formed through an $Au^{III}\rightarrow Au^{I}$ reduction process, presents a polymeric structure including Au chains with alternating Au—Au distances of 3.0898 (8) and 3.1181 (8) Å. The coordination geometry is best described on the basis of linear $[AuBr(C_6H_{11}NS)]$ molecules, which are associated into a one-dimensional polymer *via* a common aurophilic interaction.

Comment

As an extension of our work on the extractive properties of *ω*-thiocaprolactam (1-azacycloheptane-2-thione, Hthcl) in liquid–liquid separation processes, we recently directed our efforts toward gold. Au^I is classified as a soft acid and is known to coordinate to a variety of soft bases, particularly sulfur-containing ligands. For instance, thiourea gives a very stable water-soluble Au^I complex, *viz*. $[Au\{S{=}C(NH_2)_2\}_2]^+$, which is useful in the extraction of gold from ores (Chernyak *et al.*, 1979). Moreover, Au compounds with sulfur-containing ligands are of current interest owing to their fascinating structural chemistry, and due to their wide variety of applications in classical and modern technologies (Schmidbaur, Grohmann, Olmos & Schier, 1999; Schmidbaur, Grohmann & Olmos, 1999) and in medicine (Brown & Smith, 1980; Shaw, 1999). We previously reported the efficiency of Hthcl for binding late transition metals with a d^{10} electronic configuration, such as Hg^{II} (Nuñez Gaytán *et al.*, 1998) and Cd^{II} and Ag^I (Bernès *et al.*, 1999). We now report the preparation and characterization of the title compound, (I), the first Au^I complex including Hthcl as a ligand.



(I)

The asymmetric unit of (I) contains two Au^I ions, two Br^- anions and two *S*-coordinated Hthcl ligands, with all atoms lying on general positions (Fig. 1). The two Au^I cations present similar coordination geometries (Table 1). The Br and Hthcl moieties are *trans*-coordinated [Br—Au—S = 172.75 (9)° for Au1 and 170.69 (9)° for Au2] and a dimeric fragment is formed through an Au—Au single bond. These $[AuBr(Hthcl)]_2$ units are joined *via* an intermolecular Au···Au interaction [Au—Au1···Au = 143.595 (18)° and Au—Au2···Au = 148.803 (17)°], forming a one-dimensional inorganic polymer based on an $[Au1{-}Au2]_\infty$ chain running along a 2_1 axis parallel to *b* (Fig. 2). These chains are densely packed in the

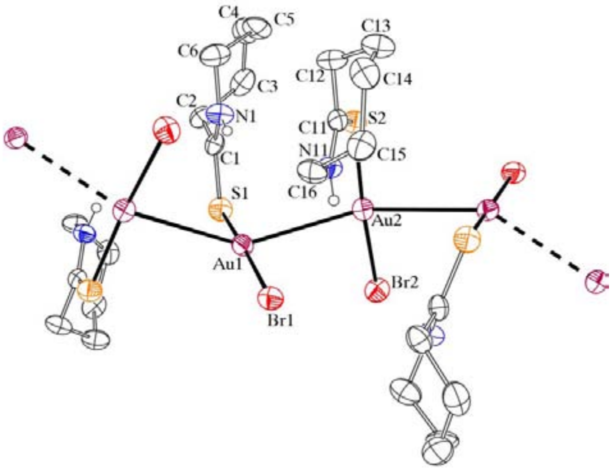


Figure 1
Part of the polymeric structure of (I), showing the atom labelling for the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level. H atoms bonded to C atoms have been omitted for clarity. Dashed bonds indicate the direction of polymerization.

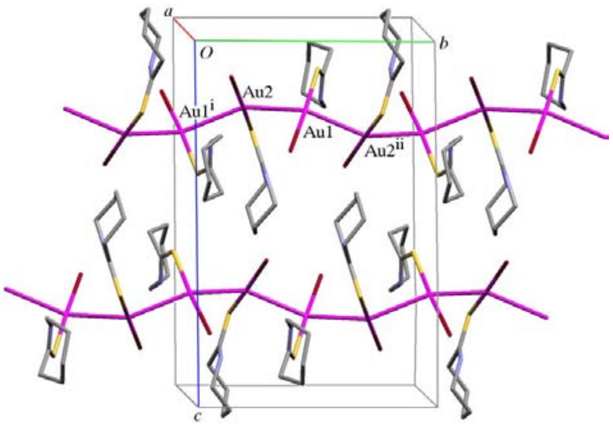


Figure 2
A view, along the *a* axis, of the unit cell of (I). H atoms have been omitted for clarity. [Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$.]

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crystalline state, reaching a packing-index of 0.706 (Spek, 2003). The two metal centres are chemically identical Au^{I} cations, as evidenced from electrochemical reduction of (I) (see *Experimental*). On the other hand, the Hthcl ligands are unaffected by the polymeric character of (I) and retain the geometry of the free ligand (Mozzhukhin *et al.*, 1993; Núñez Gaytán, 1997), characterized by a chair conformation for the seven-membered ring and an actual C=S bond [1.677 (13) and 1.689 (13) Å]; however, this bond is slightly weakened by coordination to Au, as reflected in the shift of 45 cm^{-1} for the C=S stretching vibration (see *Experimental*).

Numerous homometallic polymeric species incorporating an Au chain and monodentate ligands have been reported, which can be structurally classified as follows: with the minimal empirical formula for the complex being [AuL_1L_2], the corresponding polymer may be either a homopolymer or a copolymer, which in the crystalline state is necessarily regular. For the former class, each Au ion coordinates two different L_1 and L_2 ligands, while in the latter, Au(L_1)$_2$ and Au(L_2)$_2$ fragments alternate along the chain. The same formula may even be crystallized in both forms, as reported with L_1 = Cl and L_2 = pyridine (Jones & Ahrens, 1998). An exhaustive classification of these compounds should consider the special case $L_1 = L_2$: the resulting homopolymer is then a cationic species (*e.g.* Jiang *et al.*, 2000).

Compound (I) belongs to the homopolymer class. The arrangement of the ligands along the chain is characterized by the X—Au1—Au2—X torsion angles, where X is Br1, Br2, S1, S2 or a symmetry-related Au centre. All these angles are close to 0 or 90°. This feature extends along the polymeric chain, *i.e.* it can be observed for torsion angles about Au1—Au2^{i} [symmetry code: (i) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; Table 1]. Each independent Au atom thus apparently presents an almost square-planar geometry, with *cis* angles in the range 87.48 (4)–96.53 (9)° (Table 1). However, on the basis of orbital theory considerations, a tetrahedral geometry ($6s6p^3$-hybridized metal centre) is expected for a four-coordinate Au^{I} atom, rather than a square-planar geometry ($5d6s6p^2$ hybridization). Clearly, the actual coordination geometry around the metal centres is linear. Compound (I) consists of linear [AuBr(Hthcl)] molecules, centred on common $6s6p$-hybridized Au^{I} ions, with aurophilic (*i.e.* non-covalent) intermolecular interactions. To a certain extent, this interpretation of the X-ray structure is analogous to that used for complexes of the copolymer class. A copolymer with formula [AuL_1L_2] may be re-formulated as $[\mathrm{Au}(L_1)_2]^+\cdot[\mathrm{Au}(L_2)_2]^-$, with intermolecular aurophilic interactions. This description given for (I) is in full agreement with numerous reports on Au^{I} complexes with a linear geometry which present aurophilic interactions, a well documented phenomenon (Schmidbaur, 2000).

Some reports quantified these aurophilic interactions and concluded that they are similar in strength to hydrogen bonds, *i.e.* 7–11 kcal mol^{-1} (Schmidbaur, 1995; Harwell *et al.*, 1996; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}). From a structural point of view, it was established that two-coordinate Au^{I} complexes experience an attractive aurophilic interaction if the Au···Au separation is less than 3.6 Å (Pathaneni & Desiraju, 1993). This criterion is verified in the case of (I), with separations Au1—Au2 = 3.0898 (8) Å within the asymmetric unit and Au1—Au2^{i} = 3.1181 (8) Å for the link between asymmetric units. These values are far from the Au—Au separation reported for metallic gold (2.877 Å; Wells, 1975), but are comparable with those found in related [AuL_1L_2] polymers based on an infinite chain of Au atoms. Hitherto, three such complexes have been structurally characterized, all with L_1 = Br. With L_2 = pyridine (Conzelmann *et al.*, 1984), the Au···Au separations are 3.302 and 3.562 Å; with L_2 = *o*-xylylisocyano, one Au···Au distance is observed, of 3.348 Å (Ecken *et al.*, 1998); finally, with L_2 = tetrahydrothiophene (Ahrland *et al.*, 1993), this separation is 3.353 Å. Shorter Au—Au distances are obtained by using bridging ligands, such as thiocarbamates (Bishop *et al.*, 1998), which constrain the geometry of the Au chain (Au—Au = 2.790 and 3.157 Å for the covalent bond and the aurophilic interaction, respectively).

A careful scrutiny of these geometrical features leads to a general conclusion for (I). Assuming a direct correlation between bond length and bond strength, the Au—Au covalent bond and aurophilic interaction in (I) probably have very similar strengths. The above-mentioned range, namely 7–11 kcal mol^{-1} per Au···Au contact, thus seems to be underestimated, at least for (I) and related compounds. Another noteworthy conclusion, related to liquid–liquid extraction of gold by means of Hthcl or related sulfur-containing molecules, is that these aurophilic interactions may be sufficiently strong to persist in solution (Balch *et al.*, 1990). The ^{13}C NMR spectrum of (I) is complicated (see *Experimental*), which may result from partial decomposition into oligomers, conformational changes for Hthcl, thio-enolization of Hthcl, or a combination of these three phenomena.

Up to now, using Hthcl as ligand, we have obtained different solid-state structures with each d^{10} metal studied: monomer, cyclic oligomer or polymer. In the present case, an Au^{III}→Au^{I} reduction is observed during the course of the reaction (see *Experimental*), which is not surprising because (I) crystallizes slowly. On the other hand, the low yield obtained for a reaction which should be almost quantitative suggests the formation of other uncharacterized compounds, including Au^{III} complexes. This is supported by the isolation of a monomeric Au^{III} complex when using AuCl$_3$ (or HAuCl$_4$) as starting material (Núñez Gaytán *et al.*, 2004). A more thorough rationalization of this complex behaviour of Hthcl towards Au^{III} will be the subject of future studies.

Experimental

A 0.01 *M* solution of ω-thiocaprolactam in CHCl$_3$ was prepared. AuBr$_3$ (0.044 g, 0.1 mmol) was added to this solution (10 ml, 0.1 mmol of ω-thiocaprolactam). After stirring for 2 h at 300 K, the mixture was filtered and allowed to concentrate slowly in a test tube at 277 K. A slow rate of evaporation (several weeks) is essential for obtaining the title compound. A brown solid was collected after drying the crude product in air (yield 25.6%, 10.4 mg). Repeated crystallization of this solid by slow evaporation of an AcOEt solution at 300 K afforded suitable single crystals of (I). ATR/FT–IR (attenuated total reflectance/Fourier transform IR spectroscopy) data were obtained on a Perkin–Elmer GX equipped with a diamond ATR sampling accessory (DuraSampl IR II from SensIR Technologies): ν_{max}(C═S) = 1546 cm^{-1} for Hthcl, 1501 cm^{-1} for (I); ν_{max}(N—H) = 3170 cm^{-1} for Hthcl, 3364 cm^{-1} for (I). ^{13}C NMR (100 MHz, CH_3OD): 18 signals in the range 24.20–43.56 p.p.m. None of these signals corresponds to free Hthcl; the signal for C═S was not detected, a common feature for this class of complexes (*e.g.* Raubenheimer *et al.*, 1992). Electrochemical measurements were made using an EG&G model 273 potentiostat/galvanostat. A platinum-disc working electrode, a platinum-wire auxiliary electrode and a silver pseudo-reference electrode (immersed in the supporting electrolyte and separated from the working solution by a fritted glass disc) were used in a three-electrode configuration. All experiments were performed in 0.1 *M* TBAP (tetrabutylammonium perchlorate) in CH_2Cl_2 under a dry N_2 atmosphere at 290 K with a scan rate of 50 mV s^{-1}. The peak potential for the chemically irreversible reduction of Au^{I} to Au^{0} is −0.745 V, referenced to the observed half-wave potential for the Cp_2Fe^+/Cp_2Fe pair.

Crystal data

[AuBr($C_6H_{11}NS$)]
M_r = 406.09
Monoclinic, $P2_1/c$
a = 10.1039 (10) Å
b = 11.3131 (16) Å
c = 17.4278 (19) Å
β = 105.314 (9)°
V = 1921.4 (4) Å^3
Z = 8
D_x = 2.808 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 72 reflections
θ = 4.2–12.3°
μ = 19.62 mm^{-1}
T = 296 (1) K
Irregular prism, brown
0.32 × 0.12 × 0.10 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: refined on ΔF (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.040, T_{max} = 0.139
4490 measured reflections
3374 independent reflections
2455 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 25.0°
h = −12 → 2
k = −13 → 1
l = −20 → 20
3 standard reflections every 97 reflections intensity decay: 1.5%

Table 1
Selected geometric parameters (Å, °).

Au1—S1	2.287 (4)	S1—C1	1.677 (13)
Au1—Br1	2.4237 (15)	S2—C11	1.689 (13)
Au1—Au2	3.0898 (8)	N1—C1	1.308 (14)
Au1—Au2^{i}	3.1181 (8)	N1—C6	1.461 (16)
Au2—S2	2.282 (3)	N11—C11	1.303 (14)
Au2—Br2	2.4284 (14)	N11—C16	1.491 (15)
S1—Au1—Br1	172.75 (9)	Br2—Au2—Au1	89.03 (4)
S1—Au1—Au2	92.88 (10)	S2—Au2—Au1^{ii}	88.98 (9)
Br1—Au1—Au2	87.48 (4)	Br2—Au2—Au1^{ii}	90.11 (4)
S1—Au1—Au2^{i}	90.38 (10)	Au1—Au2—Au1^{ii}	148.803 (17)
Br1—Au1—Au2^{i}	93.62 (4)	C1—S1—Au1	110.1 (4)
Au2—Au1—Au2^{i}	143.595 (18)	C11—S2—Au2	110.8 (4)
S2—Au2—Br2	170.69 (9)	C1—N1—C6	128.1 (11)
S2—Au2—Au1	96.53 (9)	C11—N11—C16	126.4 (10)
S1—Au1—Au2—S2	86.70 (12)	Au2—Au1—Au2^{i}—Au1^{i}	78.52 (5)
Au2^{i}—Au1—Au2—S2	−7.86 (8)	Au2—Au1—Au2^{i}—Br2^{i}	−9.79 (5)
Br1—Au1—Au2—Br2	86.94 (5)	Br1—Au1—Au2^{i}—Br2^{i}	80.87 (5)
Br1—Au1—Au2—Au1^{ii}	−1.68 (5)	S1—Au1—Au2^{i}—Au1^{i}	−16.86 (9)
Au2^{i}—Au1—Au2—Au1^{ii}	91.01 (5)	S1—Au1—Au2^{i}—S2^{i}	84.09 (12)

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.106
S = 1.03
3374 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 9.115P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.51 e Å^{-3}
$\Delta\rho_{min}$ = −1.31 e Å^{-3}
Extinction correction: *SHELXL*97 in *SHELXTL-Plus* (Sheldrick, 1998)
Extinction coefficient: 0.00047 (7)

Due to the high $\mu \times R$ value for the crystal of (I), the absorption correction was applied through a ΔF refinement procedure instead of using collected ψ-scan data, which gave a somewhat worse final refinement [R_1 = 0.048 for 2455 $I > 2\sigma(I)$, *versus* R_1 = 0.043 for the refinement reported here]. The structure was first refined isotropically with all H atoms placed in idealized positions (R_1 = 0.094). *DIFABS* (Walker & Stuart, 1983) from the *WinGX* system (Farrugia, 1999) was then applied to the raw diffraction data and the model was refined to convergence. The accuracy of the applied correction is far from perfect, as evidenced by the high residual peak observed in the final difference map of 1.5 e Å^{-3} close to atom Au1. Unfortunately, the crystal shape was considered to be inappropriate for an accurate and error-free numerical absorption correction. H atoms were refined using a riding model, with constrained N—H distances of 0.86 Å and C—H distances of 0.97 Å, and with U_{iso}(H) = 1.2U_{eq}(parent atom).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus* and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1058). Services for accessing these data are described at the back of the journal.

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