positions [C—H = 0.96 Å and $U(H) = 1.2U_{eq}$ of the adjacent C atom]. The H-atom parameters were not refined.

Data collection: *XSCANS* (Siemens, 1994*b*). Cell refinement: *XSCANS*. Data reduction: *XPREP* in *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994*a*). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

One of us (MSH) is grateful to the KFUPM Dhahran, Saudi Arabia, for one year of sabbatical leave at the Chemistry Department, Texas A&M University in Dr M. Y. Darensbourg's laboratory. The X-ray diffraction and crystallographic computing system was purchased from funds provided by the National Science Foundation (USA) grant CHE-8513273.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1044). Services for accessing these data are described at the back of the journal.

References

Ahrland, S., Aurivillius, B., Dreisch, K., Norén, B. & Oskarsson, A. (1992). *Acta Chem. Scand.* **46**, 262–265.

Akhtar, M. N., Gazi, I. H., Isab, A. A., Al-Arfaj, A. R., Wazeer, M. I. M. & Hussain, M. S. (1997). *J. Coord. Chem.* **36**, 149–157.

Akhtar, M. N., Isab, A. A., Wazeer, M. I. M., Hussain, M. S. & Al-Arfaj, A. R. (1996). *J. Chem. Soc. Dalton Trans.* Accepted for publication.

Al-Arfaj, A. R., Hussain, M. S., Isab, A. A. & Akhtar, M. N. (1996). *Acta Cryst.* C**52**, 550–553.

Bellon, P. L., Manassero, M. & Sansoni, M. (1969). *La Riceus Sci.* **39**, 173–175.

Cotton, F. A. & Wilkinson, G. (1972). *Advanced Inorganic Chemistry*, 3rd ed., p. 1052. New York: John Wiley & Sons.

Duddell, D. A., Goggin, P. L., Goodfellow, R. J., Norton, M. G. & Smith, J. G. (1970). *J. Chem. Soc. A*, pp. 545–548.

Graham, G. G., Haavisto, T. M., Jones, H. M. & Champion, G. D. (1984). *Biochem. Pharmacol.* **33**, 1257–1262.

Graham, G. G., Haavisto, T. M., McNaught, P. J., Browne, C. D. & Champion, G. D. (1982). *J. Rheum.* **4**, 527–532.

Hormann, A. L., Shaw, C. F., Bennett, D. W. & Reiff, M. W. (1986). *Inorg. Chem.* **25**, 3953–3957.

Hormann-Arendt, A. L. & Shaw, C. F. III (1990). *Inorg. Chem.* **29**, 4683–4686.

Hussain, M. S., Al-Arfaj, A. R., Akhtar, M. N. & Isab, A. A. (1996). *Polyhedron*, **15**, 2781–2785.

Isab, A. A (1992). *J. Inorg. Biochem.* **45**, 145–150, and references therein.

James, D. W., Ludvigsen, N. W., Cleland, L. G. & Milazzo, S. C. (1982). *J. Rheum.* **9**, 532–537.

Reibenspies, J. H., Draper, J. D., Struck, G. & Darensbourg, D. J. (1996). *Z. Kristallogr.* **211**, 400–401.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994*a*). *XP. Interactive Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994*b*). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 1555–1558

Bis(*N*,*N*′-dimethylthiourea-*S*)gold(I) Perchlorate and Bis(*N*,*N*′-diethylthiourea-*S*)gold(I) Perchlorate

Richard J. Staples,[a] John P. Fackler Jr[b] and Juan Costamagna[c]

[a] *University of Idaho, Moscow, ID 83804, USA,* [b] *Department of Chemistry, Laboratory of Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843-3255, USA, and* [c] *Department of Chemistry, Universidad de Santiago de Chile, Santiago, Chile. E-mail: staples@chemistry.harvard.edu*

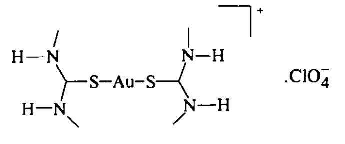
(Received 10 December 1996; accepted 3 June 1997)

Abstract

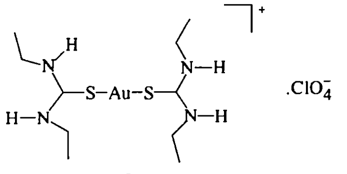
The gold(I) center in each of the title complexes, $[Au(C_3H_8N_2S)_2]ClO_4$, (1), and $[Au(C_5H_{12}N_2S)_2]ClO_4$, (2), is essentially linearly coordinated through the S atoms of the dialkylthiourea ligands. The complexes crystallize in pairs, with an Au···Au separation of 3.620 (4) and 4.294 (2) Å for (1) and (2), respectively. The perchlorate anion does not interact with the bis(alkylthiourea)gold(I) cation. Compound (1) sits on a twofold axis.

Comment

Gold(I) complexes containing sulfur ligands are of interest as medicines (Parish & Cottrill, 1987) for the control of rheumatoid arthritis in cancer chemotherapy and also for their optical and electronic properties (Puddephatt, 1978). Thiourea ligands have long been used in the recovery of heavy metals from waste solutions. We have recently structurally characterized bis(thiourea)gold(I) bromide (Porter, Fackler, Costamagna & Schmidt, 1992). Continuing these Au—S structural studies, we have characterized bis(*N*,*N*′-dimethylthiourea)gold(I) perchlorate, (1), and bis(*N*,*N*′-diethylthiourea)gold(I) perchlorate, (2).



(1)



(2)

The molecules of (1) and (2) with their atom-labeling schemes are shown in Figs. 1 and 2, respectively. The two complexes have similar values for the C—S—S—C torsion angle, 110.8 (7) and 113.4 (8)° for (1) and (2), respectively. Although compound (2) did not refine as well as expected, the fact that it has the same geometry as (1) would suggest that it has approximately the same Au· · ·Au contact; however, this distance is longer than that in complex (1). This difference must be due to packing, steric or electronic effects.

The Au—S distances and AuS$_2$ geometry in the title complexes are not significantly different from those of related complexes (Porter, Fackler, Costamagna & Schmidt, 1992). Gold(I) complexes often

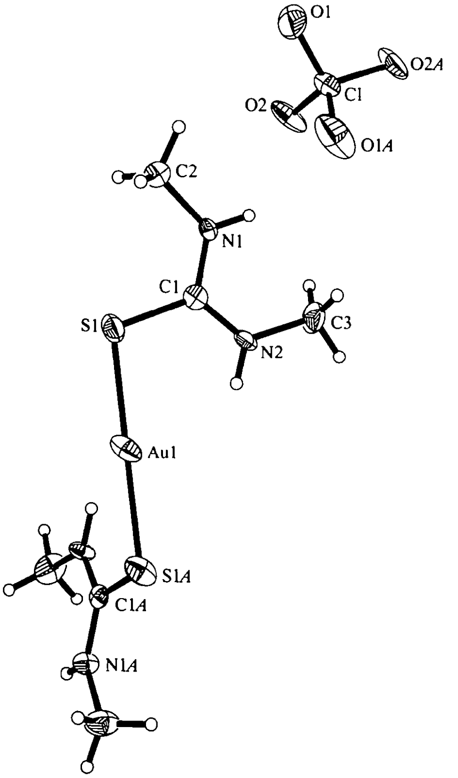


Fig. 1. A view of complex (1) showing the atom-labeling scheme, with displacement ellipsoids drawn at the 50% probability level.

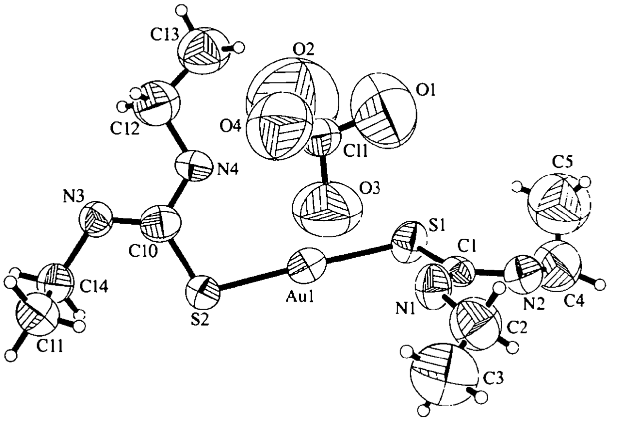


Fig. 2. A view of complex (2) showing the atom-labeling scheme, with displacement ellipsoids drawn at the 50% probability level.

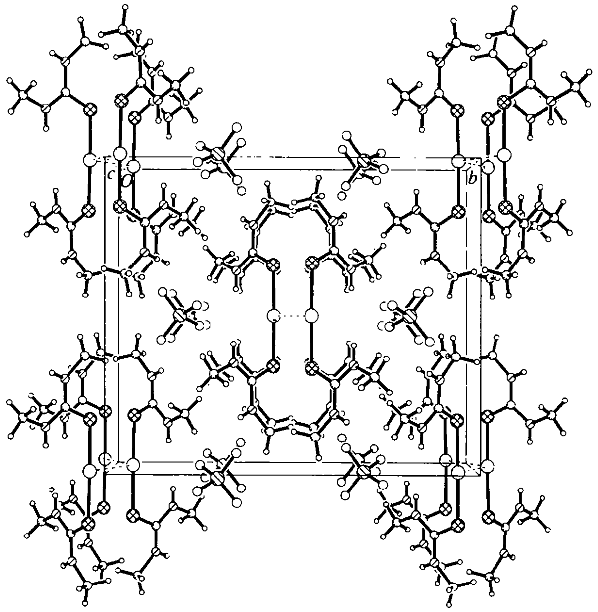


Fig. 3. A unit-cell diagram of complex (1) viewed down the *c* axis, showing the very weak Au· · ·Au interactions [3.620 (4) Å].

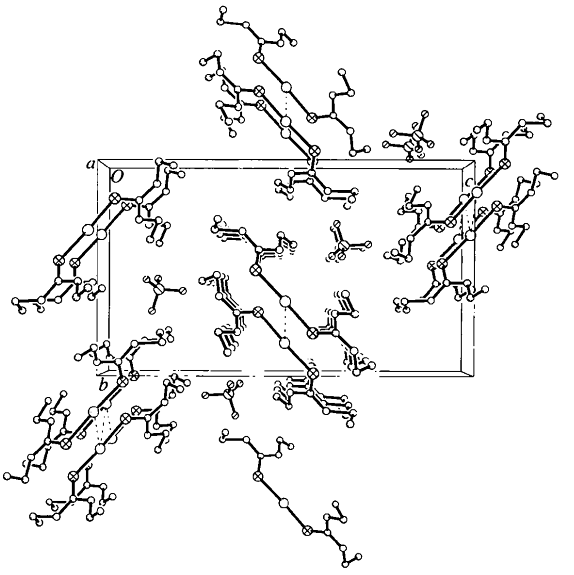


Fig. 4. A unit-cell diagram of complex (2) viewed down the *a* axis, showing the very weak Au· · ·Au interactions [4.294 (2) Å].

display Au···Au interactions (<3.3 Å) in the solid state (Dávila, Elduque, Grant, Staples & Fackler, 1993). However, linear S—Au—S-bonded cationic complexes (Table 3) have much longer Au···Au distances, with little evidence for bonding interactions. On the other hand, neutral and anionic bridged binuclear dithiocarbamate and 1,1-dithiolate species produce some of the shortest Au···Au distances observed (2.76–2.79 Å; Khan, Wang & Fackler, 1989) for gold(I) compounds.

We have recently observed that increased coordination around a gold(I) center can occur with S—Au—S angles that show a coordination with 1,2-dithiolate ligands which give an irregular three-coordinate complex (Dávila, Elduque, Grant, Staples & Fackler, 1993). The S—Au—S angles [178.67 (10) and 176.9 (4)° for (1) and (2), respectively] in the complexes reported here are essentially linear and suggest that the gold centers are only two coordinate.

Experimental

A concentrated aqueous solution of $KAuCl_4$ was added dropwise, with constant stirring, to a saturated aqueous solution of the ligand *N*,*N*′-dimethylthiourea or *N*,*N*′-diethylthiourea, in a 2:1 ligand-to-gold molar proportion. Concentrated $HClO_4$ was added to the resulting clear solution until full precipitation of a white solid occurred. This was filtered and redissolved in methanol, from which colorless needle-shaped crystals were obtained.

Compound (1)

Crystal data

$[Au(C_3H_8N_2S)_2]ClO_4$
$M_r = 504.76$
Orthorhombic
Pbcn
$a = 13.8946\ (8)$ Å
$b = 16.5130\ (1)$ Å
$c = 6.4276\ (4)$ Å
$V = 1474.8\ (2)$ Å^3
$Z = 4$
$D_x = 2.273$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3103 reflections
$\theta = 2$–$23°$
$\mu = 10.45$ mm^{-1}
$T = 293\ (2)$ K
Needle
$0.30 \times 0.15 \times 0.05$ mm
Colorless

Data collection

Siemens CCD diffractometer
ω scans
Absorption correction: semi-empirical (Blessing, 1995)
$T_{min} = 0.332$, $T_{max} = 0.593$
4437 measured reflections
1054 independent reflections
1048 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 23.26°$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 18$
$l = -7 \rightarrow 7$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.110$
$S = 1.252$
1054 reflections
83 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 9.7787P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.524$ e Å^{-3}
$\Delta\rho_{min} = -0.914$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Au1—S1	2.289 (3)	N1—C1	1.313 (9)
S1—C1	1.728 (7)	N1—C2	1.452 (10)
S1—Au1—S1^i	178.67 (10)	C1—S1—Au1	104.8 (3)

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

Compound (2)

Crystal data

$[Au(C_5H_{12}N_2S)_2]ClO_4$
$M_r = 560.87$
Orthorhombic
$P2_12_12_1$
$a = 7.278\ (1)$ Å
$b = 12.127\ (3)$ Å
$c = 21.118\ (6)$ Å
$V = 1863.7\ (8)$ Å^3
$Z = 4$
$D_x = 1.999$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1624 reflections
$\theta = 2.2$–$22.5°$
$\mu = 8.28$ mm^{-1}
$T = 193\ (2)$ K
Needle
$0.15 \times 0.05 \times 0.05$ mm
Colorless

Data collection

Siemens CCD diffractometer
ω scans
Absorption correction: semi-empirical (Blessing, 1995)
$T_{min} = 0.465$, $T_{max} = 0.661$
6226 measured reflections
2395 independent reflections
1659 reflections with $I > 2\sigma(I)$
$R_{int} = 0.106$
$\theta_{max} = 22.49°$
$h = -8 \rightarrow 5$
$k = -14 \rightarrow 14$
$l = -21 \rightarrow 24$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.092$
$wR(F^2) = 0.171$
$S = 1.116$
2395 reflections
200 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + 62.499P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.980$ e Å^{-3} (located 1.15 Å from Au)
$\Delta\rho_{min} = -1.098$ e Å^{-3} (located 1.15 Å from Au)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.14 (4)

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

Au1—S2	2.271 (9)	S2—C10	1.67 (3)
Au1—S1	2.293 (9)	N3—C10	1.32 (4)
S1—C1	1.70 (3)	N3—C14	1.53 (4)
S2—Au1—S1	176.9 (4)	C3—C2—N1	118 (4)
C1—S1—Au1	107 (1)	C1—N2—C4	126 (3)
C10—S2—Au1	108 (1)	C1—N1—C2	122 (3)

Table 3. *Selected Au···Au intermolecular distances (Å) for unsupported two-coordinate S—Au—S complexes*

Complex	Au···Au
$[Au(thiourea)_2]Br$[a]	3.40
$[Au(thiourea)_2]ClO_4$[b]	3.58
$[Au(ethylthiourea)_2]Cl.H_2O$[c]	none
$[Au\{SC(NHCH_3)OCH_2CH_3\}_2]Cl$[d]	none
$[Au(SC_5N)_2]ClO_4$[e]	3.285
$[Au\{SC(NHCH_3)_2\}_2]ClO_4$[f]	3.620 (4)
$[Au\{SC(NEt)_2\}_2]ClO_4$[f]	4.294 (2)

References: (*a*) Porter, Fackler, Costamagna & Schmidt (1992); (*b*) Chi-Chang, Shi-Xiong & Rong-Sheng (1990); (*c*) Jones, Guy & Sheldrick (1976); (*d*) Castellato, Fracasso, Grayiani, Sindellari, Gonyáles & Nicolini (1990); (*e*) Uson *et al.* (1990); (*f*) present study.

Data were collected using a Siemens SMART CCD-based (charge-coupled device) diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames was collected with a final resolution of 0.85 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using *SMART* software and refined using *SAINT* (Siemens, 1995) on all observed reflections. Data reduction was performed using the *SAINT* software which corrects for Lp and decay. Absorption corrections were applied using *SADABS* supplied by George Sheldrick based on the method of Blessing (1995). The structures were solved by direct methods using the *SHELXS*86 (Sheldrick, 1985) program and refined by the least-squares method on F^2 using *SHELXL*93 (Sheldrick, 1993), incorporated in *SHELXTL/PC* (Sheldrick, 1990). Both compounds did not diffract very well beyond 45° and these data were not used for refinement. C-bound H atoms were placed in idealized positions [C—H = 0.96 Å and U(H) = 0.08 Å^3 (fixed)]. N-bound and O-bound H atoms were located in a difference Fourier map. The H-atom parameters were not refined. Compound (2) was refined as a racemic twin using *SHELXTL/PC* software. Attempts to place the complex in a higher space group failed to give satisfactory results [Flack parameter = 0.14 (4)].

For both compounds, data collection: *ASTRO* (Siemens, 1995); cell refinement: *SMART*; molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

Support from the National Science Foundation CHE 8708625 and the Robert A. Welch Foundation is gratefully acknowledged. We would like to thank the Single-Crystal X-ray Diffraction Laboratory at the University of Idaho for data collection on the Siemens SMART CCD diffractometer system. Funding for the laboratory was provided by the NSF-Idaho EPSCoR program under NSF OSR-9350539 and the M. J. Murdock Charitable Trust, Vancouver, Washington.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Castellato, U., Fracasso, G., Grayiani, R., Sindellari, L., Gonyáles, A. S. & Nicolini, M. (1990). *Inorg. Chim. Acta*, **167**, 21–24.
Chi-Chang, L., Shi-Xiong, L. & Rong-Sheng, Y. J. (1990). *Struct. Chem.* pp. 9–11.
Dávila, R. M., Elduque, A., Grant, T., Staples, R. J. & Fackler, J. P. Jr (1993). *Inorg. Chem.* **32**, 1749–1755.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jones, P. G., Guy, J. J. & Sheldrick, G. M. (1976). *Acta Cryst.* B**32**, 3321–3322.
Khan, Md. N. I., Wang, S. & Fackler, J. P. Jr (1989). *Inorg. Chem.* **28**, 3579–3588.
Parish, R. V. & Cottrill, S. M. (1987). *Gold Bull.* **20**, 3–8.
Porter, L. C., Fackler, J. P. Jr, Costamagna, J. & Schmidt, R. (1992). *Acta Cryst.* C**48**, 1751–1754.
Puddephatt, R. J. (1978). In *The Chemistry of Gold.* Amsterdam: Elsevier.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XP. Interactive Molecular Graphics Program.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1995). *ASTRO* and *SAINT. Data Collection and Processing Software for the SMART System.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Uson, R., Laguna, A., Laguna, M., Jiménez, J., Gómez, M. P., Sainz, A. & Jones, P. G. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3457–3463.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1036). Services for accessing these data are described at the back of the journal.

Acta Cryst. (1997). C**53**, 1558–1561

Poly{guanidinium bis[dichloromercury(II)]-μ_4-chloro}

Maciej Kubicki[a] and Marek Szafrański[b]

[a]*Laboratory of Crystallography, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and* [b]*Faculty of Physics, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland. E-mail: mkubicki@chem.amu.edu.pl*

(*Received 5 February 1997; accepted 27 May 1997*)

Abstract

Both the $[C(NH_2)_3]^+$ cations and the $[Hg_2Cl_5]^-$ anions of the title compound occupy special positions on two different twofold axes, one passing through the central Cl atom of the anion (along [100]), the other along a C—N bond of the cation (along [010]). The coordination polyhedron around the Hg atom can be described as