Reaction Products between Gold(III) Bromide and Tetramethylthiourea: Dibromobis(tetramethylthiourea)gold(III) Dibromoaurate(I) and Bromo(tetramethylthiourea)gold(I). Synthesis, Crystal and Molecular Structure, and Infrared Spectra†

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The compounds dibromobis(tetramethylthiourea)gold(III) dibromoaurate(I), $[Au(tmtu)_2Br_2][AuBr_2]$, and bromo(tetramethylthiourea)gold(I), $[Au(tmtu)Br]$ were prepared and characterized by means of *X*-ray diffraction. The crystals of $[Au(tmtu)_2Br_2][AuBr_2]$ are triclinic, space group $P\bar{1}$, (C_i^1, no. 2) with a = 8.223(1), b = 9.987(1), c = 8.078(1) Å, α = 105.74(1), β = 117.20(1), γ = 84.35(1)°, and Z = 2; the crystals of $[Au(tmtu)Br]$ are monoclinic, space group $P2_1/c$, (C_{2h}^5, no. 14) with a = 6.999(1), b = 19.898(1), c = 8.044(1) Å, β = 115.75(1)°, and Z = 4. The structures were solved by the heavy-atom method, and least-squares refinement of structural parameters led to a conventional R factor of 0.034 (R' = 0.034) for 1 677 and R = 0.028 (R' = 0.029) for 1 271 independent reflections for $[Au(tmtu)_2Br_2][AuBr_2]$ and $[Au(tmtu)Br]$ respectively. The compound $[Au(tmtu)_2Br_2][AuBr_2]$ is ionic. The structure consists of centrosymmetric units in which the two gold atoms are four- and two-co-ordinated, respectively. The ligand is *trans*-co-ordinated to the gold(III) of the cationic part of the compound, together with two bromine atoms forming a square-planar geometry; the anionic part is formed by linearly co-ordinate dibromoaurate(I). The structure of $[Au(tmtu)Br]$ consists of two-co-ordinated gold(I) units. Each tetramethylthiourea is bonded by the sulphur atom. Infrared bands are diagnostic of the co-ordination environments around the metal atoms.

It is known that in reactions of thiourea derivatives with oxidizing agents one molecule of formamidine disulphide is formed for every two of thiourea present initially.[1–4] The oxidant may be chlorine, bromine, iodine, hydrogen peroxide, *etc.* or metals such as Ir^{IV}, Os^{VIII}, Te^{IV}, or Fe^{III}.[5–8] We have proposed the same reaction to occur in the presence of gold(III). Our results, however, are different from those of other authors, in fact we have obtained not only the oxidized compound but also complexes with the unoxidized thiourea whether with gold(III) or gold(I).

Experimental

All chemicals were of a reagent grade and used as received.

Solid tetramethylurea (tmtu) (2.3 mmol) was added to a solution of Au_2O_3 (0.5 mmol) in EtOH (8 cm^3) + 48% HBr (0.35 cm^3). A red compound was formed within 24 h. The crystals of $[Au(tmtu)_2Br_2][AuBr_2]$ (**1**) were filtered off and washed with EtOH–EtOEt (1:1); recrystallization was from dimethylformamide (dmf)–EtOH (1:1) using EtOH–n-hexane (1:2) as precipitant. Diethyl ether (28 cm^3) was added to the mother-liquor and 6 h later pale yellow needle-shaped crystals were formed. The crystals of octamethyldithiobisformamidinium dibromide (**2**), $(C_5H_{12}N_2SBr)_2{\cdot}2H_2O$, were washed with diethyl ether. n-Hexane (15 cm^3) was added to the solution until a light opalescence was formed. Six days later colourless crystals of $[Au(tmtu)Br]$ (**3**) were formed, filtered off, and washed with Et_2O [Found: C, 12.4; H, 2.5; N, 5.6; S, 6.7. Calc. for $C_{10}H_{24}Au_2Br_4N_4S_2$, (**1**): C, 12.3; H, 2.5; N, 5.7; S, 6.6. Found: C, 26.1; H, 6.3; N, 12.3; S, 13.6. Calc. for $C_{10}H_{28}Br_2N_4O_2S_2$, (**2**): C, 26.1; H, 6.1; N, 12.2; S, 13.9. Found: C, 14.6; H, 3.1; N, 7.0; S, 7.7. Calc. for $C_5H_{12}AuBrN_2S$, (**3**): C, 14.7; H, 3.0; N, 6.9; S, 7.8%]. In the described preparation, with the ratio Au:tmtu = 3:7, part of the ligand is complexed and part is oxidized. Yields: 42.1, 18.6, and 9.6% for (**1**), (**2**), and (**3**) respectively. Carbon, hydrogen, nitrogen, and sulphur were determined with a Carlo Erba 1106 elemental analyser.

The i.r. spectra were recorded in the solid state with a Bruker IFS 113v Fourier-transform spectrophotometer using KBr pellets in the 4 000—400 cm^{-1} region and polyethylene pellets in the 400—40 cm^{-1} region.

Crystallography.—Crystal data. $C_{10}H_{24}Au_2Br_4N_4S_2$, M = 987.0, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 8.223(1), b = 9.987(1), c = 8.078(1) Å, α = 105.74(1), β = 117.20(1), γ = 84.35(1)°, U = 567.68(1) Å^3, D_m = 2.87 g cm^{-3} (by flotation), Z = 2, D_c = 2.89 g cm^{-3}, $F(000)$ = 442, graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 195.1 cm^{-1}, crystal dimensions *ca.* 0.10 × 0.20 × 0.20 mm.

Unit-cell parameters were derived from least-squares fit to the setting angles of 25 intense reflections in the range θ 6—15°. The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer with the ω—2θ scan technique in the range 2—28°, at a scan speed range of 1.0—5.5° min^{-1}, with a scan width 0.7° + 0.35 tanθ. Two standard reflections were measured every 3 h, and the intensities showed no significant changes. 2 923 Reflections collected, 1 803 observed, 1 677 unique with $I > 3.0\ \sigma(I)$ (after merge R = 0.015); number of parameters 103; $\Delta\rho$ = 1.3 (maximum) and −1.2 (minimum) e Å^{-3} near the heavy atoms.

$C_5H_{12}AuBrN_2S$, M = 409.09, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 6.999(1), b = 19.898(1), c = 8.044(1) Å, β = 115.75(1)°, U = 1 009.04(3) Å^3, D_m = 2.70 g cm^{-3} (by flotation), Z = 4, D_c = 2.69 g cm^{-3}, $F(000)$ = 744, μ(Mo-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final positional parameters

Atom	X/a	Y/b	Z/c
(*a*) $[Au(tmtu)_2Br_2][AuBr_2]$			
Au(1)	0.0	0.5	0.5
Au(2)	0.0	0.0	1.0
Br(1)	0.221 5(3)	0.341 7(2)	0.635 3(3)
Br(2)	0.149 9(2)	0.174 9(2)	0.956 0(2)
S	0.269 0(4)	−0.003 3(3)	1.281 1(5)
N(1)	0.309(1)	−0.192(1)	1.469(1)
N(2)	0.294(1)	−0.279(1)	1.167(1)
C(1)	0.287(1)	−0.173(1)	1.306(2)
C(2)	0.416(2)	−0.303(1)	1.551(2)
C(3)	0.237(2)	−0.097(2)	1.591(2)
C(4)	0.331(2)	−0.261(1)	1.011(2)
C(5)	0.235(2)	−0.421(1)	1.136(2)
(*b*) $[Au(tmtu)Br]$			
Au	0.206 39(6)	0.176 29(2)	0.325 48(6)
Br	0.311 0(2)	0.065 50(6)	0.284 2(2)
S	0.085 5(4)	0.277 4(1)	0.367 8(4)
N(1)	0.452(1)	0.338 7(4)	0.421(1)
N(2)	0.141(1)	0.393 8(4)	0.237(1)
C(1)	0.238(1)	0.340 6(4)	0.340(1)
C(3)	0.582(1)	0.370 3(6)	0.342(2)
C(5)	0.230(2)	0.460 1(6)	0.272(2)
C(2)	0.570(1)	0.296 8(6)	0.582(1)
C(4)	−0.078(1)	0.390 6(6)	0.094(1)

Table 2. Bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

(*a*) $[Au(tmtu)_2Br_2][AuBr_2]$			
Au(1)–Br(1)	2.358(2)	Au(2)–Br(2)	2.420(1)
Au(2)–S	2.342(3)	C(1)–S	1.74(1)
C(1)–N(1)	1.30(1)	C(2)–N(1)	1.45(1)
C(3)–N(1)	1.46(1)	C(1)–N(2)	1.34(1)
C(4)–N(2)	1.48(1)	C(5)–N(2)	1.46(1)
S–Au(2)–Br(2)	87.6(1)	C(1)–S–Au(2)	106.5(3)
C(2)–N(1)–C(1)	124(1)	C(3)–N(1)–C(1)	122(1)
C(3)–N(1)–C(2)	114(1)	C(4)–N(2)–C(1)	123(1)
C(5)–N(2)–C(1)	122(1)	C(5)–N(2)–C(4)	113(1)
N(1)–C(1)–S	119(1)	N(2)–C(1)–S	120(1)
N(2)–C(1)–N(1)	121(1)		
(*b*) $[Au(tmtu)Br]$			
Au–Br	2.391(1)	Au–S	2.265(2)
C(1)–S	1.727(9)	C(1)–N(1)	1.35(1)
C(2)–N(1)	1.46(1)	C(3)–N(1)	1.45(1)
C(1)–N(2)	1.33(1)	C(4)–N(2)	1.46(1)
C(5)–N(2)	1.43(1)		
S–Au–Br	175.4(1)	C(1)–S–Au	109.6(3)
C(2)–N(1)–C(1)	121.4(8)	C(3)–N(1)–C(1)	123.4(8)
C(3)–N(1)–C(2)	114.7(8)	C(4)–N(2)–C(1)	122.1(8)
C(5)–N(2)–C(1)	123.1(8)	C(5)–N(2)–C(4)	114.2(8)
N(1)–C(1)–S	122.5(7)	N(2)–C(1)–S	118.8(6)
N(2)–C(1)–N(1)	118.7(8)		

K_α) = 180.6 cm^{-1}, crystal dimensions *ca.* 0.10 × 0.10 × 0.20 mm.

Unit-cell parameters were derived from least-squares fit to the setting angles of 25 intense reflections in the range θ 9—15°. The intensity data were collected as above at a scan speed range of 1.0—4.1° min^{-1}. Two standard reflections were measured every 4 h, and the intensities showed no significant changes. 2 676 Reflections collected, 1 364 observed, 1 271 unique with $I > 3.0\,\sigma(I)$ (after merge $R = 0.024$); number of parameters 91; $\Delta\rho = 0.8$ (maximum) and -1.0 (minimum) e Å^{-3} near the heavy atoms.

All data were corrected for Lorenz and polarization effects, and an empirical absorption correction, based on the Ψ scan, was applied[9] {maximum, minimum transmission factors = 0.99, 0.26 and 0.99, 0.55 for $[Au(tmtu)_2Br_2][AuBr_2]$ and $[Au(tmtu)Br]$ respectively}.

The structures were solved by conventional Patterson and Fourier methods, and refined by full-matrix least-squares calculations, with $\Sigma w(|F_o| - F_c|)^2$ being minimized. Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were treated as fixed contributors at calculated positions assuming a bond distance of 1.0 Å and a thermal parameter 1 Å^2 greater than that of the attached carbon atom. The positions of the hydrogen atoms were calculated assuming C–N–C–H torsion angles of +180, −60, and +60°. This model converged at $R = 0.034$ and $R' = 0.034$, $w = 1.4/[\sigma^2(F) + 0.0003F_o^{\,2}]$ for $[Au(tmtu)_2Br_2][AuBr_2]$ and at $R = 0.028$ and $R' = 0.029$, $w = 1.0/[\sigma^2(F) + 0.000\,35F_o^{\,2}]$ for $[Au(tmtu)Br]$ {the unweighted and weighted residuals are defined as: $R = \Sigma(|F_o| - F_c|)/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}.

During refinement of $[Au(tmtu)Br]$ zero weights were assigned to three low-order reflections, which may be affected by secondary extinction.

Complex neutral-atom scattering factors[10] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76[11] program package and the ORTEP[12] plotting program.

The collection of data for octamethyldithiobisformamidinium dibromide failed because of decomposition of the crystalline matter under *X*-ray radiation.

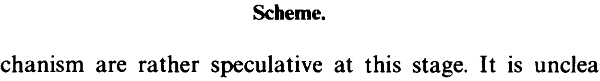
Final fractional co-ordinates for non-hydrogen atoms are given in Table 1, bond distances and angles in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The observed results are not surprising. Indeed tetramethylthiourea is expected to undergo substitution reactions with tetrabromoaurate(III) as well as to act as a reducing agent towards the same chemical species. Our experimental results indicate that both processes occur yielding *trans*-dibromobis(tetramethylthiourea)gold(III) dibromoaurate(I) (**1**), bromo(tetramethylthiourea)gold(I) (**3**), and octamethyldithiobisformamidinium dibromide (**2**) as reaction products.

trans-Effect considerations justify the formation and the subsequent isolation of (**1**). Complex (**3**) involves thiourea, and the product of reduction of gold(III), (**2**), is the stable product of oxidation processes involving thiourea and its analogues, according to the Scheme. Considerations on the overall reaction mechanism are rather speculative at this stage. It is unclear whether the observed reaction products are controlled by a favourable balance of the free-energy changes or are controlled by the kinetics of the chemical system. Research on related systems is in progress in this Laboratory in order to elucidate this aspect.



Scheme.

Description of the Structures.—The crystal structure of

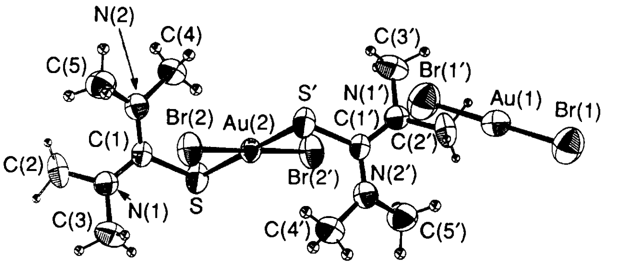


Figure 1. ORTEP view of the $[\mathrm{Au(tmtu)_2Br_2}][\mathrm{AuBr_2}]$ complex showing the atom numbering and thermal motion ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

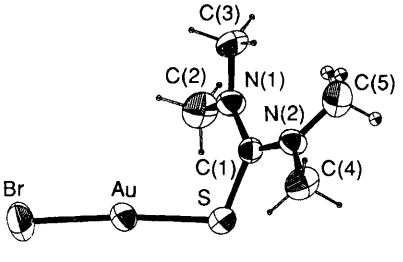


Figure 2. ORTEP view of the [Au(tmtu)Br] complex showing the atom numbering and thermal motion ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

$[\mathrm{Au(tmtu)_2Br_2}][\mathrm{AuBr_2}]$, Figure 1, consists of two ions containing gold(III), two tetramethylthiourea molecules, and two bromine atoms, and gold(I) and two bromine atoms, respectively. In the cationic part of the complex salt the $\mathrm{Au^{III}}$–Br and $\mathrm{Au^{III}}$–S(tmtu) bond distances 2.420(1) and 2.342(3) Å, respectively, are very close to those reported.[13,14] The $\mathrm{Au^{I}}$–Br bond distance 2.358(2) Å of the anionic part of the complex is very similar to that of bis(*N*,*N*-di-n-butyldithiocarbamato)-gold(III) dihalogenoaurate(I) at 2.349(5) Å.[15]

The gold(III) and gold(I) are in special positions, so that the co-ordination polyhedra have crystallographic imposed symmetry, planar and linear, respectively. The cation gold has a planar but not regular square environment. The angles S–Au–Br are 87.6(1) and 92.4(1)°. The shortest van der Waals contacts are between S and N(1) $(1 - x, -y, 3 - z)$ at 3.564(4) Å and Br(2) and N(2) $(-x, -y, 2 - z)$ at 3.451(4) Å.

The crystal structure of [Au(tmtu)Br], Figure 2, consists of monomeric units in which the gold(I) atom exhibits the usual linear co-ordination. The $\mathrm{Au^{I}}$–Br bond distance at 2.391(1) is similar to those found previously, 2.387(2) and 2.377(6) Å.[16,17] The $\mathrm{Au^{I}}$–S bond distance at 2.265(2) Å is very close to those found in bis(ethylenethiourea)gold(I) chloride hydrate.[18,19] All bond distance values are shorter than those involving $\mathrm{Au^{III}}$, due to the different oxidation state of the metal. The $\mathrm{Au^{I}}$–S bond distance is shorter than expected for a purely σ bond (the sum of the covalent radii is 2.36 Å[20,21]) and, as already suggested,[22] probably involves a small measure of d_π–d_π bonding. The S–Au–Br angle is 175.4(1)°, the deviation from linearity being attributable to a weak contact between S and Au $(x, 1.5 - y, 0.5 + z)$ at 3.523(4) Å.

Vibration Spectra.—The fact that *trans* co-ordination occurs in the gold(III) cation is well detected in the i.r. spectrum by the two bands at 320 and 258 cm^{-1} assignable to a large contribution from the stretching vibrations of $\mathrm{Au^{III}}$–S and $\mathrm{Au^{III}}$–Br respectively. These results are in good accord with the observed metal–bromine stretching vibrations for *trans*-$[\mathrm{AuBr_2L_2}]$ complexes in the solid state.[23]

Taking into account that the stretching vibrations rise with increasing oxidation number of the metal, implying that the MX force constant is greater the higher the oxidation number of the metal, and that, on the other hand, the higher the co-ordination number, the lower is the frequency, the final result is a small increase in frequencies for $\mathrm{Au^{III}}$–X compared to $\mathrm{Au^{I}}$–X (X = S or Br), as $\mathrm{Au^{I}}$–Br of the anionic part of the molecule is unequivocally observed at 235 cm^{-1}.

In the case of [Au(tmtu)Br] the two stretching bands of $\mathrm{Au^{I}}$–S and $\mathrm{Au^{I}}$–Br are at 285[24] and 228 cm^{-1},[25] respectively.

Acknowledgements

We are grateful to the Ministero della Pubblica Istruzione (M. P. I.) of Italy for grants, to the Centro Interdipartimentale di Calcolo Automatico ed Informatica Applicata (C.I.C.A.I.A.) of Modena University for computer facilities, and to the Centro Interdipartimentale Grandi Strumenti of Modena University for recording of spectra and intensity data collection.

References

1 H. N. Po, H. Eran, Y. Kim, and J. E. Byrd, *Inorg. Chem.*, 1979, **18**, 197.
2 M. Hoffmann and J. O. Edwards, *Inorg. Chem.*, 1977, **16**, 3333.
3 Z. Amjad and A. McAuley, *Inorg. Chim. Acta*, 1977, **25**, 127.
4 F. Cristiani and A. Diaz, *Inorg. Chim. Acta*, 1977, **24**, L7.
5 U. Russo, S. Calogero, N. Burrieschi, and M. Petrera, *J. Inorg. Nucl. Chem.*, 1979, **41**, 25.
6 U. Russo, S. Calogero, and G. Valle, *Cryst. Struct. Commun.*, 1980, **9**, 829.
7 U. Russo, G. Valle, and S. Calogero, *J. Chem. Soc., Dalton Trans.*, 1980, 2303.
8 O. Foss, J. Johnsen, and O. Tvedten, *Acta Chem. Scand.*, 1958, **12**, 1782.
9 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 105 and 174.
11 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
12 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
13 M. A. Bennett, K. Hoskins, W. R. Kneen, R. S. Nyholm, P. B. Hitchcock, R. Mason, G. B. Robertson, and A. D. C. Towl, *J. Am. Chem. Soc.*, 1971, **18**, 4591.
14 J. H. Noordik, W. Hummelink, and J. G. M. Van der Linden, *J. Coord. Chem.*, 1973, **2**, 185.
15 P. T. Beurskens, J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, 1968, **7**, 805.
16 J. Stahle, W. Hiller, and W. Conzelmann, *Z. Naturforsch., Teil B*, 1984, **39**, 538.
17 F. W. B. Einstein and R. Restivo, *Acta Crystallogr., Sect. B*, 1975, **31**, 624.
18 P. G. Jones, J. J. Guy, and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1976, **32**, 3321.
19 P. A. Bates and J. M. Waters, *Acta Crystallogr., Sect. C*, 1985, **41**, 862.
20 T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1971, 1685.
21 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
22 M. G. Drew and M. J. Riedl, *J. Chem. Soc., Dalton Trans.*, 1973, 52.
23 L. H. Jones, *Inorg. Chem.*, 1964, **3**, 1581.
24 R. Battistuzzi and G. Debbi, *Transition Met. Chem. (Weinheim, Ger.)*, 1976, **1**, 248.
25 G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.

Received 7th *March* 1990; *Paper* 0/01033B