Synthesis and Spectroscopic and Structural Properties of Mercury(II) Tetramethylthiourea Complexes. Crystal Structure of Di-μ-bromo-bis-[bis(tetramethylthiourea-*S*)mercury(II)] Tetrafluoroborate

By **Luigi Pietro Battaglia** and **Anna Bonamartini Corradi**, Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., University of Parma, 43100 Parma, Italy
Giuseppe Marcotrigiano, Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy
Gian Carlo Pellacani,* Istituto di Chimica Generale ed Inorganica, University of Modena, 41100 Modena, Italy

The structure of the title complex has been determined by *X*-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions a = 12.554(6), b = 10.737(6), c = 8.362(4) Å, α = 111.93(2), β = 90.63(5), γ = 105.88(6)°, Z = 1; R = 0.046. The structure comprises discrete $[\{Hg(tmtu)_2Br\}_2]^{2+}$ binuclear cations and $[BF_4]^-$ anions (tmtu = tetramethylthiourea). Each mercury(II) atom is four-co-ordinated by two sulphur and two bromine atoms, the bromines bridging two mercury(II) atoms to give a dimer. Also prepared and investigated are complexes of the type $[\{Hg(tmtu)_2X\}_2]Y_2$ ($X \neq Y$, X = Cl or Br, Y = BF_4 or ClO_4; X = Y = BF_4 or ClO_4) and $Hg(tmtu)_4Y_2$. The i.r. spectra (60—4 000 cm^{-1}) of all the complexes show shifts of the characteristic tetramethylthiourea bands suggesting co-ordination of the ligand through the sulphur atom. In the far-i.r. spectra of the complexes, metal–sulphur and halide bands have been assigned on the basis of C_i and T_d symmetry for the $[\{Hg(tmtu)_2X\}_2]Y_2$ and $Hg(tmtu)_4Y_2$ complexes, respectively.

As part of a study on mercury complexes with ' soft ' ligands, such as thiourea and substituted thioureas,[1,2] a series of complexes have been prepared and studied by physico-chemical measurements: $Hg(tmtu)_2X(Y)$ (tmtu = tetramethylthiourea; $X \neq Y$, X = Cl or Br, Y = BF_4 or ClO_4; X = Y = BF_4 or ClO_4), and $Hg(tmtu)_4Y_2$ (Y = BF_4 or ClO_4). The crystal structure of $Hg(tmtu)_2Br(BF_4)$ has been determined by *X*-ray crystallography.

EXPERIMENTAL

Preparation of the Complexes.—The complex $Hg(tmtu)_2(BF_4)_2$ was prepared by adding a warm (40—50 °C) methanol–water (5 cm^3 : 5 cm^3) solution of tetramethylthiourea (2 mmol) and HBF_4 (30%) (1 cm^3) to a warm solution (10 cm^3) of HgO in HBF_4 (30%). The perchlorate complex was prepared similarly, using $HClO_4$ (70%). It was precipitated immediately, whereas the fluoroborate was obtained by cooling (4—5 °C) for 24 h. Both complexes were recrystallized from absolute ethanol.

The complexes $Hg(tmtu)_4Y_2$ (Y = BF_4 or ClO_4) were obtained by treating the $Hg(tmtu)_2Y_2$ complexes (1 mmol) in methanol (5 cm^3) with a tetramethylthiourea (2 mmol) solution in methanol (5 cm^3). The products were recrystallized from methanol by cooling. The mixed complexes $Hg(tmtu)_2X(Y)$ (X = Cl or Br; Y = BF_4 or ClO_4) were prepared by dissolving the $Hg(tmtu)_2Y_2$ complexes (1.5 mmol) in methanol (15 cm^3) and adding a stoicheiometric amount of LiCl or NaBr in methanol (3 cm^3). The complexes precipitated on cooling at 4—5 °C.

The analyses and melting points for all the complexes are in Table 1.

Physical Measurements.—The i.r. spectra of NaCl or KBr pellets (400—4 000 cm^{-1}) and far-i.r. spectra of Nujol mulls (60—500 cm^{-1}) were recorded on a Perkin-Elmer 180 spectrophotometer. Nitrogen, carbon, and hydrogen were determined using a Perkin-Elmer 240 elemental analyser.

Crystal Data.—The unit-cell dimensions were determined from rotation and Weissenberg photographs and refined using an ' on-line ' single-crystal Siemens diffractometer by accurate measurements of some high-angle reflections, $[\{Hg(tmtu)_2Br\}_2][BF_4]_2$, Triclinic, M = 1 263.6, a = 12.554(6), b = 10.737(6), c = 8.362(4) Å, α = 111.93(2), β = 90.63(5), γ = 105.88(6)°, U = 997.5(9) $Å^3$, D_m = 2.12, Z = 1, D_c = 2.10 g cm^{-3}, $F(000)$ = 600, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 96.12 cm^{-1}, space group $P\bar{1}$.

TABLE 1

Analytical results and melting points

Complex	Analysis (%) *			M.p. (θ_c/°C)
	C	H	N	
$Hg(tmtu)_2Cl(BF_4)$	20.8	4.35	9.30	123—127
	(20.45)	(4.10)	(9.54)	
$Hg(tmtu)_2Br(BF_4)$	18.95	4.05	8.70	121—125
	(19.0)	(3.80)	(8.85)	
$Hg(tmtu)_2(BF_4)_2$	19.05	3.95	9.30	153—157
	(18.8)	(3.80)	(8.75)	
$Hg(tmtu)_4(BF_4)_2$	26.8	5.45	12.45	152—156
	(26.6)	(5.35)	(12.4)	
$Hg(tmtu)_2Cl(ClO_4)$	20.35	4.40	9.2	125—129
	(20.0)	(4.05)	(9.35)	
$Hg(tmtu)_2Br(ClO_4)$	18.3	3.65	8.35	109—113
	(18.6)	(3.75)	(8.70)	
$Hg(tmtu)_2(ClO_4)_2\cdot 4H_2O$	16.4	4.00	7.65	208—212
	(16.3)	(4.40)	(7.60)	
$Hg(tmtu)_4(ClO_4)_2$	26.25	5.30	12.5	146—150
	(25.85)	(5.20)	(12.05)	

* Calculated values are given in parentheses.

Data collection. Intensity data were collected from a prismatic crystal of length 0.76 mm and of cross section 0.05 × 0.06 mm, aligned with the c axis parallel to the ϕ axis of a Siemens AED diffractometer. A total of 3 481 reflections was measured in the range $5 < 2\theta < 54°$, using the Mo-K_α radiation and ω—2θ scan technique; 1 308 reflections were considered unobserved, having intensities $I < 3\sigma(I)$, and were not used in the analysis. The intensity of a standard reflection monitored every 20 reflections did not vary significantly during the data collection. Correction for Lorentz and polarization effects, but not for absorption, were applied. Data were placed on an absolute scale, first by correlating observed and calculated structure amplitudes, then by determining the scale factors for the F_o values as parameters in the least-squares refinement.

Structure analysis. The co-ordinates of the mercury atom were readily obtained from a Patterson map. The electron-density distribution calculated by including the mercury gave the positions of all the non-hydrogen atoms. The atomic co-ordinates were refined by least squares assuming anisotropic thermal parameters for Hg, Br, and S, and isotropic parameters for N, C, B, and F. The function minimized was $\Sigma w|F_o - F_c|^2$ in which the weighting for each reflection was unity. The final *R* value was 0.046.

Positional parameters are given in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22446 (17 pp.).* Atomic scattering factors employed in the calculations were taken from ref. 3 with correction for the real and imaginary part for mercury, bromine, and sulphur from ref. 4. All the calculations were performed on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale.

TABLE 2

Final fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses for $[\{Hg(tmtu)_2Br\}_2][BF_4]_2$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Hg	635(1)	4 185(1)	1 304(1)
Br	704(1)	6 897(2)	2 086(2)
S(1)	2 326(4)	3 873(5)	118(7)
S(2)	−845(3)	3 523(4)	2 911(7)
F(1)	2 808(20)	779(25)	2 927(31)
F(2)	4 614(11)	1 218(14)	2 789(18)
F(3)	3 837(17)	1 936(21)	5 201(29)
F(4)	3 895(16)	2 990(22)	3 573(26)
N(1)	3 432(11)	6 439(13)	2 466(18)
N(2)	3 799(11)	5 916(15)	−366(20)
N(3)	−49(11)	1 506(14)	3 106(19)
N(4)	−1 968(12)	902(15)	2 275(20)
C(1)	3 251(11)	5 562(15)	833(21)
C(2)	3 194(16)	5 669(21)	3 911(28)
C(3)	3 728(16)	8 015(21)	3 003(27)
C(4)	3 422(19)	5 180(24)	−2 230(32)
C(5)	4 951(17)	6 963(22)	148(29)
C(6)	−948(13)	1 828(16)	2 709(22)
C(7)	980(16)	2 567(21)	4 189(27)
C(8)	−4(19)	18(24)	2 244(31)
C(9)	−2 299(18)	−160(23)	3 096(30)
C(10)	−2 864(20)	1 055(25)	1 326(32)
B	3 740(24)	1 721(31)	3 413(40)

TABLE 3

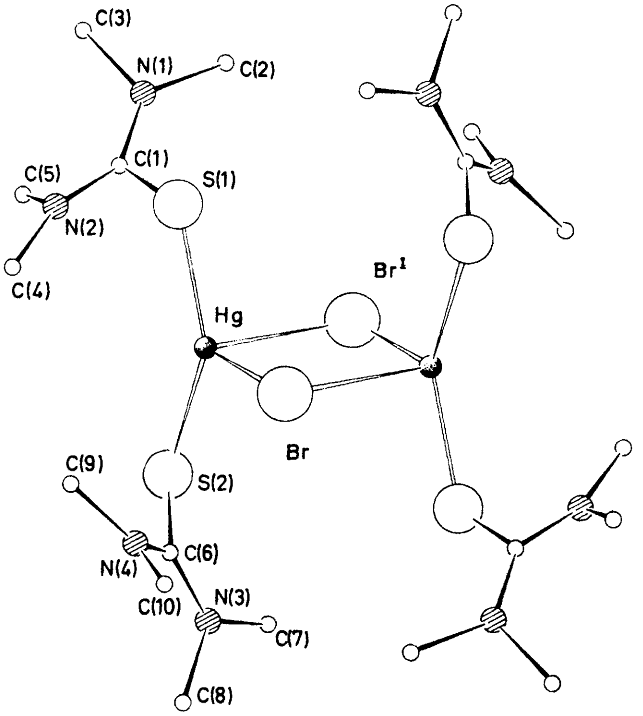
Bond distances (Å) and angles (°) in the cation $[\{Hg(tmtu)_2Br\}_2]^{2+}$ with estimated standard deviations in parentheses

Hg–Br	2.712(5)	Hg–S(1)	2.406(9)
Hg–Br^{I} [a]	2.929(4)	Hg–S(2)	2.410(7)
S(1)–C(1)	1.74(2)	S(2)–C(6)	1.73(2)
C(1)–N(1)	1.31(2)	C(6)–N(3)	1.34(2)
C(1)–N(2)	1.33(2)	C(6)–N(4)	1.33(2)
N(1)–C(2)	1.48(3)	N(3)–C(7)	1.48(3)
N(1)–C(3)	1.51(3)	N(3)–C(8)	1.51(3)
N(2)–C(4)	1.46(3)	N(4)–C(9)	1.51(3)
N(2)–C(5)	1.51(3)	N(4)–C(10)	1.45(3)
Br–Hg–S(1)	107.6(1)	Br–Hg–Br^{I}	94.6(1)
Br–Hg–S(2)	100.0(1)	Br^{I}–Hg–S(1)	94.8(1)
S(1)–Hg–S(2)	148.5(2)	Br^{I}–Hg–S(2)	98.0(1)
Hg–S(1)–C(1)	104.7(6)	Hg–S(2)–C(6)	107.0(6)
S(1)–C(1)–N(1)	122(1)	S(2)–C(6)–N(3)	121(1)
S(1)–C(1)–N(2)	116(1)	S(2)–C(6)–N(4)	117(1)
N(1)–C(1)–N(2)	121(1)	N(3)–C(6)–N(4)	122(2)
C(1)–N(1)–C(2)	123(2)	C(6)–N(3)–C(7)	123(2)
C(1)–N(1)–C(3)	122(2)	C(6)–N(3)–C(8)	119(2)
C(2)–N(1)–C(3)	114(2)	C(7)–N(3)–C(8)	117(2)
C(1)–N(2)–C(4)	123(2)	C(6)–N(4)–C(9)	120(2)
C(1)–N(2)–C(5)	120(2)	C(6)–N(4)–C(10)	122(2)
C(4)–N(2)–C(5)	116(2)	C(9)–N(4)–C(10)	116(2)
In the $[BF_4]^-$ anions [b]			
B–F(1)	1.26(4)	F(1)–B–F(2)	113(3)
B–F(2)	1.38(3)	F(1)–B–F(3)	98(3)
B–F(3)	1.42(4)	F(1)–B–F(4)	124(3)
B–F(4)	1.28(4)	F(2)–B–F(3)	105(2)
		F(2)–B–F(4)	113(2)
		F(3)–B–F(4)	99(3)

[a] The roman numeral superscript I indicates the symmetry equivalent position $\bar{x}$, $1 - y$, $\bar{z}$. [b] For the $[BF_4]^-$ anions, having very high thermal parameters, there is a poor degree of reliability in the bond distances and angles.

RESULTS AND DISCUSSION

Crystal Structure.—Table 3 lists bond distances and angles. The structure determination revealed in the crystals discrete $[\{Hg(tmtu)_2Br\}_2]^{2+}$ binuclear cations and $[BF_4]^-$ anions. As shown in the Figure, in the cation two bromine atoms, related by a centre of symmetry, bridge two mercury atoms. In this way, the metal is four-co-ordinated by two sulphur atoms, and two bromine atoms one of which is at a longer distance. The structure of the cation can be also described as a highly distorted edge-condensed tetrahedron. The mercury atom is displaced out of the plane S(1), S(2), Br by 0.26 Å. The bond angles at the metal range from 94.8 to 148.5°. The Hg–S distances are intermediate between the sum of the digonal covalent radii (2.34 Å) and the tetrahedral covalent radii (2.52 Å) [5] and within the range of the Hg–S distances usually found.[6-12] The Hg–Br distances are comparable with those formed when the



Clinographic projection of the cation

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

bromine atom is bridging.[13] In both ligand molecules the thiourea groups are planar, as can be seen from the least-squares planes (Table 4); the dihedral angle between the mean planes S(1), C(1), N(1), N(2) and S(2), C(2), N(4), N(5) is 89.8°. Corresponding dimensions for each of the ligands are similar; as expected, the S–C distances are significantly shorter than calculated (1.81 Å),[14] but similar to the value (1.72 Å) for the free thiourea [15] and several of its derivatives and co-ordination complexes, and are normal for sp^2 hybridized carbon. Bond angles at sulphur in the complex are Hg–S(1)–C(1) 104.7 and Hg–S(2)–C(6) 107.0°, respectively, and those around the sulphur-bonded carbon do not differ significantly from 120°.

TABLE 4

Least-squares planes and deviations (Å) of atoms from these planes in square brackets. The equations of the least-squares planes are in the form $AX + BY + CZ = D$, where X, Y, and Z are co-ordinates (Å) referred to orthogonal axes, obtained from fractional co-ordinates by applying the matrix:

$$\begin{array}{cccc} a\sin\gamma & 0 & -c\sin\alpha\cos\beta^{*} \\ a\cos\gamma & b & c\cos\alpha \\ 0 & 0 & c\sin\alpha\sin\beta^{*} \end{array}$$

	A	B	C	D
Plane (1): S(1), S(2), Br [Hg 0.257(1), Br^{I} 3.184(2)] *	−0.464 5	0.104 0	−0.879 4	−1.033 5
Plane (2): S(1), C(1), N(1), N(2) [S(1) −0.001(5), C(1) 0.009(16), N(1) −0.004(14), N(2) −0.005(16)]	−0.717 2	0.674 2	−0.176 5	0.218 6
Plane (3): S(2), C(6), N(3), N(4) [S(2) −0.001(5), C(6) 0.027(17), N(3) −0.012(14), N(4) −0.014(15)]	0.281 0	0.052 8	−0.958 3	−2.345 1

* The roman numeral superscript I indicates the symmetry-equivalent position $\bar{x}, 1 - y, \bar{z}$.

The packing is determined by van der Waals contacts (Table 5).

TABLE 5

Contacts <3.5 Å

F(1)–C(7)	3.32(3)	F(2)–C(10^{II})	3.43(3)
F(1)–C(8)	3.39(3)	F(1)–C(3^{III})	3.49(4)
F(1)–C(10^{I})	3.37(3)	F(3)–C(9^{IV})	3.08(3)
F(4)–C(2)	3.46(3)	F(3)–C(3^{V})	3.37(3)

Symmetry-equivalent positions:

I $\bar{x}, \bar{y}, \bar{z}$
II $1 + x, y, z$
III $x, 1 - y, z$
IV $\bar{x}, \bar{y}, 1 - z$
V $1 - x, 1 - y, 1 - z$

Infrared Spectra.—In the light of the crystal structure of the $[\{Hg(tmtu)_2Br\}_2][BF_4]_2$ complex, since the principal bands of the i.r. spectra (Table 6) of all the complexes are shifted in the same direction with respect to those of the free ligand, it is reasonable to suggest co-ordination of the thiourea ligand through the sulphur atom in all the complexes. In fact the ligand band at 1 503 cm^{-1} (ν_1) assigned [16] to 89% ν_{asym}(CN) +11% δ(NCS) is shifted in the complexes to higher energies, while the bands at 1 410 (ν_2), 660 (ν_3), and 480 cm^{-1} (ν_4), assigned to 37% ν_{sym}(CN) +25% ν(CS) +23% δ(NCN) +15% δ_{sym}(NMe), 53% ν_{sym}(C′N) +47% ν_{asym}(C′N), and 63% ν_{asym}(NMe) +38% ν_{asym}(C′N) respectively,[16] are shifted to lower energies on complexation. The ligand bands at 1 031 and 990 cm^{-1} having an appreciable contribution from ν(CS) are obscured in the complexes by the $[BF_4]^-$ and $[ClO_4]^-$ bands. Since the vibrational spectra of the $[\{Hg(tmtu)_2X\}_2]Y_2$ (X = Cl or Br, Y = BF$_4$ or ClO$_4$; X = Y = BF$_4$ or ClO$_4$) complexes are similar to one another and to the structurally known $[\{Hg(tmtu)_2Br\}_2][BF_4]_2$ complex, we suggest that they also have similar structures. This may be strictly true for $[\{Hg(tmtu)_2X\}_2]Y_2$ (X = Cl or Br, Y = BF$_4$; X = Br, Y = ClO$_4$) complexes, which are isomorphous and exhibit identical *X*-ray powder spectra.

The study of the vibrational spectra of the $[BF_4]^-$ and $[ClO_4]^-$ anions is complicated since in this spectral region some ligand bands also appear. However, some differences in the anion spectral region can be observed between the $[\{Hg(tmtu)_2X\}_2]Y_2$ and $Hg(tmtu)_4Y_2$ complexes and the $[\{Hg(tmtu)_2Y\}_2]Y_2$ complexes (X = Cl or Br, Y = BF$_4$ or ClO$_4$). In particular, the presence of multiple bands at 1 000—1 150 and 600—650 cm^{-1} in the latter complexes indicates a lowering of the anion symmetry, suggesting that at least two of the four anions are co-ordinated probably by bridging two metal ions.[17]

Observed far-i.r. spectra of the complexes are reported in Table 7. The point group of the $[\{Hg(tmtu)_2X\}_2]^{2+}$ cations is C_i. This arrangement would allow two A_u

TABLE 6

Infrared spectra (cm^{-1}) of the ligand and of the complexes

Compound	ν_1	ν_2	ν_3	ν_4
tmtu	1 503s	1 410vs	660w	480m
$[\{Hg(tmtu)_2Cl\}_2][BF_4]_2$	1 570vs	1 378vs	652vw	485w, 465m
$[\{Hg(tmtu)_2Br\}_2][BF_4]_2$	1 570vs	1 378vs	652vw	488w, 466m
$[\{Hg(tmtu)_2(BF_4)\}_2][BF_4]_2$	1 580vs	1 388vs	652vw	460w
$Hg(tmtu)_4(BF_4)_2$	1 558vs	1 372vs	650w	470w
$[\{Hg(tmtu)_2Cl\}_2][ClO_4]_2$	1 560vs	1 389, 1 376vs	650w	485w, 465m
$[\{Hg(tmtu)_2Br\}_2][ClO_4]_2$	1 568vs	1 388, 1 376vs	650w	487w, 467m
$[\{Hg(tmtu)_2(ClO_4)\}_2][ClO_4]_2\cdot 4H_2O$	1 555vs	1 388, 1 376vs	650vw	490vw, 468m
$Hg(tmtu)_4(ClO_4)_2$	1 550vs	1 370vs		450m

TABLE 7

Far-i.r. spectra (cm^{-1}) of the ligand and of the complexes

Compound	ν(Hg–S)	ν(Hg–X)	Other bands ($< 400\ cm^{-1}$)
tmtu			394ms, 300m, 276ms,br, 200m, 91m
$[\{Hg(tmtu)_2Cl\}_2][BF_4]_2$	235m, 210 (sh)	184s,br	398 (sh), 387ms, 350w, 333m, 307m, 133s, 85ms, 70 (sh)
$[\{Hg(tmtu)_2Br\}_2][BF_4]_2$	240w, 210m,br	132vs,br	400 (sh), 385ms, 350w, 330m, 305m, 92m, 65ms
$[\{Hg(tmtu)_2(BF_4)\}_2][BF_4]_2$	255 (sh), 230m,br		400s, 358m, 321m, 295m, 144m, 107s, 88 (sh)
$Hg(tmtu)_4(BF_4)_2$	197s,br		397mw, 383m, 306s,br, 283s,br, 230 (sh), 113w,br, 75m,br
$[\{H(tmtu)_2Cl\}_2][ClO_4]_2$	235m,br	182s,br	400 (sh), 389ms, 332 (sh), 310ms, 275 (sh), 148m, 121w, 89w
$[\{Hg(tmtu)_2Br\}_2][ClO_4]_2$	238w, 210m	131ms,br	397 (sh), 386ms, 329w, 305mw, 280 (sh), 123w, 93w, 66m
$[\{Hg(tmtu)_2(ClO_4)\}_2][ClO_4]_2\cdot 4H_2O$	245mw, 235mw		397m, 354mw, 321m, 295mw, 149w, 112m,br, 80m
$Hg(tmtu)_4(ClO_4)_2$	196s		398s, 384m, 308m,br, 284m,br, 225 (sh)

i.r.-active and two A_g Raman-active stretching modes of the bridging halides and terminal mercury–sulphur bands. Two metal–sulphur bands are observed in the 230—275 cm^{-1} region in agreement with literature data,[2,18,19] while only one strong and broad band, which probably includes the second theoretically possible mode, is observed at 182—184 and 131—132 cm^{-1} for the chloride and bromide complexes, respectively. The low energy of the metal–halogen bands is consistent with bridging halides.

In the $Hg(tmtu)_4X_2$ ($X = BF_4$ or ClO_4) complexes the presence of only one mercury–sulphur band agrees with a tetrahedral configuration for these complexes.

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