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Monoorganomercury and diorganothallium derivatives of 2-thiouracil and 2-*S*-methylthiouracil; crystal structure of methylmercury(II)-2-*S*-methylthiouracilate

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Abstract

Monometallated derivatives of thiouracil (H_2Tu) and 2-*S*-methylthiouracil (HTuSMe), (R_nMHTu and $R_nMTuSMe$, R = Me or Ph, M = Hg or Tl) and dimetallated derivatives of 2-thiouracil [$(RHg)_2Tu$] (R = Me or Ph) have been prepared. The structure of MeHgTuSMe was determined by X-ray diffraction. The crystal was found to consist of MeHgTuSMe units, with the mercury atom bonded to nitrogen N(3) of the 2-thiouracil ring. Weak intra- and inter-molecular interactions between the metal atoms and the carbonyl group or the N(1) atom were also observed. Possible structures for the other compounds isolated are discussed on the basis of their IR, Raman and NMR (^1H, ^{13}C and ^{199}Hg) spectra.

Introduction

In earlier work [1] the coordination chemistry of RHg^+ and R_2Tl^+ cations were compared with the aim of recognising differences which might throw light on their dissimilar toxicological behaviour [2].

The reactions of these cations with heterocyclic derivatives able to undergo thiol-thione tautomerism showed them to cause varying extents of tautomeric conversion depending on the nature of the cation [1]. Organothallium compounds

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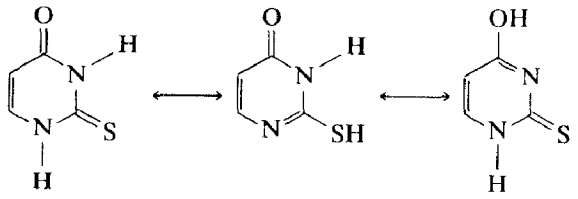
caused a weaker shift towards the thiol form by forming strong bonds to deprotonated N–H groups, suggesting that they are "harder" Lewis acid in terms of Pearson's terminology [3] than organomercury derivatives.

A subsequent step in this research involved the use of organic molecules involved in more complex tautomeric equilibria, so allowing clearer observation of coordination differences between the two types of organometallic cations. 2-Thiouracil (2,3-dihydro-2-thioxo-4(1*H*)pyrimidinone, H_2Tu) is an interesting species in this respect; since its several tautomeric forms, three of which are represented below, allow a range of coordination possibilities, and so their coordination chemistry has been studied by use of various acceptors, including $MeHg^+$ and $PhHg^+$ [4].



Such tautomeric complexity, however, complicates recognition of the nature of the coordination by the usual spectroscopic techniques. This led us to undertake a study of the monoorganomercury and diorganothallium compounds described below by:

(1) including an analysis of the coordination behaviour of the *S*-methyl-2-thiouracil (2-methylthio-4(1*H*)pyrimidinone, HTuSMe), in which the tautomerism is restricted by methylation;

(2) including dimetallated compounds;

(3) using various spectroscopic techniques in conjunction, in the solid state (IR and Raman spectroscopy) and in solution (IR and multinuclear magnetic resonance);

(4) making use of X-ray diffraction whenever possible.

The results so obtained are discussed below. The structure of Me_2TlHTu was reported previously [5], and a preliminary account of that of MeHgTuSMe has appeared [6].

Experimental

H_2Tu, MeHgAc and $[(MeHg)_3O]OH$ were obtained commercially. HTuSMe, Me_2TlI and Ph_2TlBr were prepared as described elsewhere [7].

Synthesis of the compounds

The RHgHTu and $(RHg)_2Tu$ compounds were prepared by mixing solutions of RHgAc in methanol with solutions of H_2Tu in the same solvent in molar ratios of 1/1 and 2/1, respectively.

The compound MeHgTuSMe was obtained by treating 1.87 g (0.0027 mol) of $[(MeHg)_3O]OH$ in 70 ml of methanol with an equimolar amount of HTuSMe in the same solvent. The resultant solution was concentrated until crystals appeared, some of which were used for the X-ray study. PhHgTuSMe was prepared similarly from PhHgAc.

Table 1

Analyses, colours, and melting points of the compounds

Compound	Analysis (Found (calcd.) (%))		Colour	M.p. (°C)
	C	H		
MeHgHTu	17.5 (17.5)	1.8 (1.8)	white	170 (dec)
$(MeHg)_2Tu$	13.1 (12.9)	1.4 (1.5)	white	235 (dec)
MeHgTuSMe	20.2 (20.2)	2.3 (2.3)	white	150
PhHgHTu	29.7 (29.7)	2.0 (2.0)	white	210 (dec)
$(PhHg)_2Tu$	28.0 (28.2)	1.7 (1.8)	white	225
PhHgTuSMe	31.4 (31.5)	2.5 (2.4)	white	150
Me_2TlHTu	19.9 (19.7)	2.6 (2.7)	white	200
Ph_2TlHTu	38.7 (39.6)	2.8 (2.7)	white	150
$Ph_2TlTuSMe$	44.3 (44.8)	2.7 (2.8)	white	255

The compounds Me_2TlHTu [5], Ph_2TlHTu and $Ph_2TlTuSMe$ were made by slowly adding the corresponding organometal hydroxide (obtained by treatment of the corresponding organometallic halide with an aqueous suspension of freshly prepared Ag_2O) to an alcoholic (methanol or ethanol) solution of an equimolar amount of the ligand (H_2Tu or HTuSMe). Once isolated, the solids were washed with the solvent and vacuum dried over $CaCl_2$ or P_4O_{10}.

Elemental analyses of the mercury compounds were performed by Galbraith Lab., Inc. (Knoxville, TN, U.S.A.). The thallium compounds were analysed with a Perkin–Elmer 250B apparatus. The analytical and some physical data for the compounds are given in Table 1. The integrals of the ^1H NMR spectral signals were consistent with the proposed formulae.

Spectra

Mass spectra. The mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C). All the ions included in Tables 2 and 3 were identified by use of DS-90 software.

Infrared spectra. The infrared spectra were recorded as Nujol mulls, KBr pellets, or DMSO solutions on a Perkin–Elmer 180 spectrometer, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å).

Crystal structure determination

While selecting a crystal for the X-ray study we noticed that the crystals were present in two well-defined crystal habits, one involving three pairs of opposing parallel faces (type I) and the other one pair of opposing non parallel faces (type II). The study of the type II crystals provided consistent crystallographic results, except

Table 2

Mass spectra (EI) of methylmercury(II) derivatives [a]

Ion	m/z [b]			Relative abundance [c]		
	MeHgHTu	MeHgTuSMe	$(MeHg)_2Tu$	MeHgHTu	MeHgTuSMe	$(MeHg)_2Tu$
[M]	344	358	558	78	5.7	62
[M − Me]	–	–	543	–	–	13
$[S(HgMe)_2]$	–	–	464	–	–	22
[S(HgMe)Hg]	–	–	449	–	–	9.2
$[Hg_2Me]$	–	–	417	–	–	< 5.0
$[Hg_2]$	–	–	402	–	–	< 5.0
[M − HgMe + H]	–	–	344	–	–	17
[M − SMe + H]	–	312	–	–	–	5.3
[M − HgMe − S]	–	–	311	–	–	35
[HgMe]	217	217	217	39	12	100
[Hg]	202	202	202	51	11	34

[a] Only ions containing mercury are included. [b] Nominal values calculated using the most abundant isotope ^{202}Hg. [c] Base peak: [L − S − H] (for MeHgHTu), [L − H] (for MeHgTuSMe) and [MeHg] (for $(MeHg)_2Tu$); L = ligand.

for an unusual sulphur–carbon interatomic distance for the SMe group. We are currently trying to obtain new crystals of this type with a view to establishing whether the differences are real. Subsequently below we refer to type I crystals only.

To optimize X-ray absorption corrections a few small crystals were ground by use of an instrument resembling that described by Schuyff and Hulscher [8]. A spherical crystal of 0.14 mm radius thus obtained was mounted on an Enraf–Nonius CAD-4 diffractometer. The cell dimensions, given in Table 4, were obtained by the least squares procedure from 25 reflections (2θ range, 22.82–44.06°). Intensities were measured by the ω–2θ scan technique at a rate between 6.7 and 20.0° min^{-1}. Reflections were collected over the range $0° < \theta < 26°$ ($-10 \leq h \leq 10$, $0 \leq k \leq 11$, $0 \leq l \leq 13$), using graphite monochromated Mo-K_α radiation (λ 0.71073 Å). An overall 1685 independent reflections were collected (R_{sym} 0.017 Laue equivalents after absorption correction). A spherical absorption correction was applied (maximum and minimum transmission factors 0.069 and 0.041, respectively). The intensity of standard reflection 4 1 2 varied by ±2.1% throughout the experiment. Data

Table 3

Mass spectra (EI) of R_2Tl^{III} compounds [a]

Ion	m/z [b]			Relative abundance [c]		
	Me_2TlHTu	Ph_2TlHTu	$Ph_2TlTuSMe$	Me_2TlHTu	Ph_2TlHTu	$Ph_2TlTuSMe$
[M]	362	–	500	3.3	–	2.4
[M − R]	347	409	423	25	< 1.0	19
[M − 2R]	332	332	346	7.8	< 1.0	4.5
$[TlR_2]$	235	359	359	28	7.8	36
[TlR]	220	–	282	7.7	–	3.2
[Tl]	205	205	205	100	31	100

[a] Only ions containing thallium are included. [b] Nominal values calculated using the most abundant isotope ^{205}Tl. [c] Base peak for Ph_2TlHTu: [Ph + H].

Table 4

Crystal data and diffraction details for MeHgTuSMe

Crystal class	Monoclinic
Space group	$P2_1/n$
Formula	$C_6H_9HgN_2OS$
a (Å)	8.284(1)
b (Å)	9.501(2)
c (Å)	10.976(2)
β (°)	96.88(2)
V (Å^3)	857.7(5)
D_x (g cm^{-3})	2.771
μ (mm^{-1})	18.13
λ (graphite-monochromated Mo-K_α)	0.71073
Measured unique reflections	1685
With $I > 3\sigma(I)$	919
Final R, R_w	0.037, 0.043

were corrected for Lorentz and polarization effects and their standard deviations were estimated from counting statistics.

The Hg atom was readily located on Patterson map, and all other non hydrogen atoms were then found by difference Fourier syntheses. The $\Sigma w(|F_o| - |F_c|)^2$ function, where $w = [\sigma^2(F_o) + cF_o^2]^{-1}$, with $c = 0.0016$, was minimized by anisotropic least squares. An extinction parameter, χ, defined by $F_{cor} = F_c(1 - \chi F_c^2)$, was included in the refinements ($\chi = 2.5 \times 10^{-7}$). No hydrogen atoms were included in the model. $R = 0.037$, $R_w = 0.043$ from 919 reflections, with $I > 3\sigma(I)$; 101 parameters were refined, $S = 10.3$.

In the final difference syntheses $\Delta\rho$ excursions between 1.51 and 1.43 e Å^{-3} were carried out. Final shifts/e.s.d. were all less than 0.05. Atomic scattering factors and corrections for anomalous dispersions were taken from Cromer and Waber [9] and Cromer and Ibers [10], respectively. Calculations were carried out with by use the SHELX76 [11] and SDP programs [12]. Tables of thermal parameters and final structure factors are available from the authors.

Results and discussion

Mass spectra

Table 2 list the chief characteristics of the mass spectra of the methylmercury(II) compounds. The parent ion [M] was detected in all cases and carried a large part of the ion current in the two 2-thiouracil compounds. The *S*-methylated thiouracil compound was much the less stable, as was expected since the organometallic cation has less affinity for deprotonated N–H ligands than for deprotonated S–H ligands. $(MeHg)_2Tu$ was surprisingly stable, but underwent evident loss of an [MeHg] group to leave the 1/1 complex. There was also a large abundance of $[S(MeHg)_2]$ ions and some dinuclear ions possibly derived from them.

The phenylmercury (II) compounds are much less stable under electron bombardment. The parent ion was observed unequivocally only in the case of PhHgHTu (3.5% of the [L – S] base peak). The most abundant metal-containing ions were $[Ph_2Hg]$, [PhHg], and [Hg].

The spectrum of Me_2TlHTu (Table 3) also shows the molecular ion but, in keeping with the weakness of its intermolecular interactions [5], there were no polymetallated ions such as were seen in the case of dimethyl(2-mercaptopyridinate)thallium(III) [1c]. Except for this feature these two compounds exhibit very similar ionization patterns. It is noteworthy that whereas Ph_2TlHTu only produced low-mass metal-containing ions, $Ph_2TlTuSMe$ showed $[M]^+$ ions in high abundance; this difference in behaviour may be due to the fact that *S*-methylated thiouracil complex is more volatile and less strongly associated, and reveals the considerable stability of the Tl–N bond.

X-ray structure

Figure 1 shows the atom numbering scheme, Table 5 lists the fractional atomic coordinates, and Tables 6 and 7 show the most significant bond lengths and angles.

The compound consists of molecules in which mercury is bonded to the ligand via the N(3) atom of the ring. This bond, together with the Hg–C bond of the Me(1) group, forms a virtually linear linkage (N(3)–Hg–Me(1), 176.3(5)°). The selection of N(3) rather than N(1) atom in forming the new bond is consistent with the results of charge distribution studies for the thiol form of the 2-thiouracil ligand [13]. As one would expect, the pyrimidine ring shows the most marked modifications compared with free 2-thiouracil (thione form [14]) in respect of the N(1)–C(2) and C(2)–N(3) bonds, which are significantly shorter in the complex.

The structure shows two further weak interactions (Fig. 1). First, there is an intramolecular contact with the carbonyl group. The Hg · · · O distance is shorter than that observed for (theophyllinato)methylmercury(II) monohydrate [15] and somewhat smaller than the sum of the Van der Waals radii (1.73 [16] + 1.50 Å [17]). This type of intramolecular interaction is rather uncommon in methylmercury(II) compounds [18] and probably, as with dipivaloylacetoxymercurymethane [18], arises

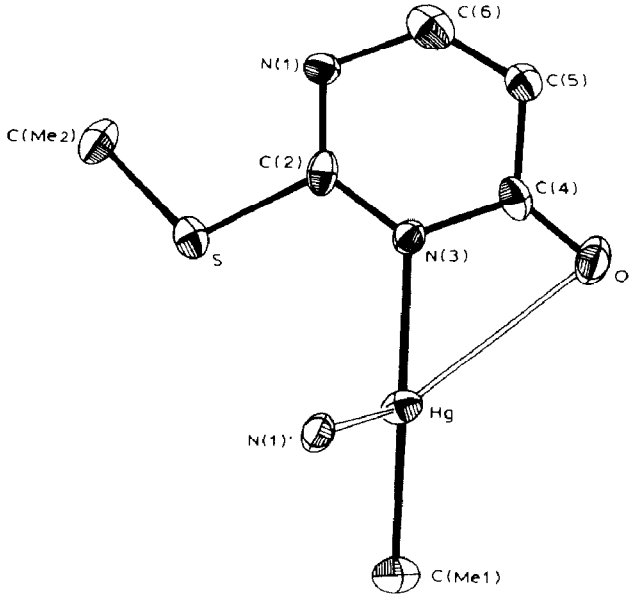


Fig. 1. Molecular structure of MeHgTuSMe and atom numbering scheme.

Table 5

Final fractional atomic coordinates and equivalent isotropic temperature factors for MeHgTuSMe (e.s.d. in brackets)

	x	y	z	B_{iso}
Hg	0.8512(1)	1.2543(1)	0.9136(1)	2.92(2)
S	0.6345(5)	0.9622(5)	0.8841(4)	4.0(1)
O	1.152(1)	1.166(1)	0.824(1)	4.3(4)
N(1)	0.879(1)	0.815(2)	0.816(1)	2.8(4)
N(3)	0.924(1)	1.055(1)	0.853(1)	2.3(4)
C(2)	0.838(2)	0.940(2)	0.849(1)	2.8(5)
C(4)	1.078(2)	1.056(2)	0.822(1)	3,1(5)
C(5)	1.135(2)	0.922(2)	0.785(1)	3.0(5)
C(6)	1.037(2)	0.814(2)	0.787(1)	3.9(6)
C(Me(1))	0.783(2	1.446(2)	0.985(1)	4.2(6)
C(Me(2))	0.576(2)	0.788(2)	0.932(2)	3.8(6)

Table 6

Interatomic distances (Å) in MeHgTuSMe [a]

Hg–N(3)	2.12(1)
Hg–C(Me(1))	2.09(2)
S–C(2)	1.79(1)
S–C(Me(2))	1.82(2)
O–C(4)	1.21(2)
N(1)–C(2)	1.30(2)
N(1)–C(6)	1.38(2)
N(3)–C(2)	1.30(2)
N(3)–C(4)	1.36(2)
C(4)–C(5)	1.43(2)
C(5)–C(6)	1.31(2)
Hg · · · O	2.91(2)
Hg · · · N(1)′	3.03(2)

[a] N(1)′ obtained from N(1) by $1.5-x$, $0.5+y$, $1.5-z$.

Table 7

Bond angles (°) in MeHgTuSMe

N(3)–Hg–C(Me(1))	176.3(5)
C(2)–S–C(Me(2))	104.2(7)
C(2)–N(1)–C(6)	111.0(1)
Hg–N(3)–C(2)	125.8(9)
Hg–N(3)–C(4)	112.5(9)
C(2)–N(3)–C(4)	122.0(1)
S–C(2)–N(1)	117.0(1)
S–C(2)–N(3)	115.0(1)
N(1)–C(2)–N(3)	128.0(1)
O–C(4)–N(3)	119.0(1)
O–C(4)–C(5)	126.0(1)
N(3)–C(4)–C(5)	115.0(1)
C(4)–C(5)–C(6)	118.0(1)
N(1)–C(6)–C(5)	127.0(1)

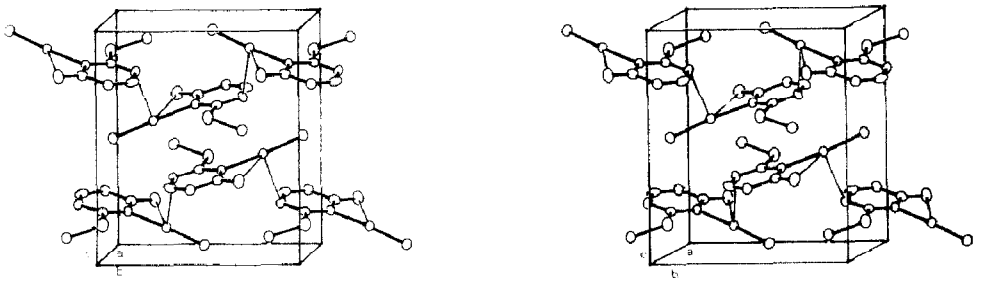


Fig. 2. Stereoview of the structure of MeHgTuSMe showing weak intra- and inter-molecular interactions.

from the ligand rigidity. A slightly shorter intramolecular contact was reported previously [19]. It is impossible to decide whether the carbon–oxygen distance undergoes a significant change with respect to that in the free ligand [14] because of the high e.s.d. of this parameter in this structure, but the Hg–N(3)–C(4) angle is clearly smaller than H–N(3)–C(4) angle in free 2-thiouracil [14].

Secondly, the N(1)′ ··· Hg distance (Table 6, Fig. 2) is also smaller than the sum of the Van der Waals radii (1.73 [16] + 1.55 Å [17]), which suggests the presence of a very weak intermolecular interaction that leads the molecules of the complex to form a pseudochain along crystallographic axis *b* (Fig. 2).

IR spectra

(a) Analysis of the ligand vibrations. Table 8 list the positions of the bands of H_2Tu which undergo the most significant shifts upon methylation and/or coordination. As can be seen, there are some clear trends which warrant some comments.

Table 8

Major bands in the IR spectra of H_2Tu, HTuSMe, and its complexes [a]

H_2Tu	1680vs, b	1560vs		1445s	1235s	1000m	910m	840s
MeHgHTu	1670vs	1520vs		1455m	1265vs, b	980vs	925m	845m
	1650s						915m	
$(MeHg)_2Tu$	1620m	1540m		1440sh	1310vs	1005vs	940m	825s
	1590vs	1520w			1270w			
PhHgHTu	1590vs	1540s		1470m	1270vs	1015w	935m	790vs
				1450m	1240m			850m
$(PhHg)_2Tu$	1620vs			1470m	1310vs	1020m	940m	815vs
	1610vs					1005s		825m
Me_2TlHTu	1675vs	1550m		1490vs	1245vs	995vs	920m	820sh
	1650sh			1470s				
Ph_2TlHtu	1540vs, b	1570m		1470m	1280vs	1015m	930w	820s
						995s		
HTuSMe	1660vs, b	1570s	1540s	1460s	1290s	980vs	925m	825s
MeHgTuSMe	1615vs	1570sh	1550w	1450vs	1315s	1000s	930w	840s
	1600sh				1305s			
PhHgTuSMe	1610vs, b	1580sh	1550w	1460vs	1320vs	1005s	935m	820s
	1600sh				1310vs			
$Ph_2TlTuSMe$	1560vs	1570m	1540m	1440vs	1330vs	990s	945m	815s
			1520s					

[a] w = weak; s = strong; m = medium; b = broad; sh = shoulder; vs = very strong.

Upon the methylation, the deprotonation and thione-thiol transformation give rise to shifts of about 20 cm^{-1} in the band appearing at 1680 cm^{-1} in H_2Tu (ν(C=O) [20]), and that on the one hand confirms the observations made on other systems [21] and, on the other emphasizes the need to proceed cautiously in diagnosing involvement of the C=O group in coordination to the metal on the basis of shifts of this band to smaller wavenumbers, particularly when the shifts are small. The methylation also causes shifts in the H_2Tu bands at 1560, 1445, 1235 and 1000 cm^{-1} (ring stretching [20]), 910 cm^{-1} (τ(CH) [20]) and 840 cm^{-1} (α(ring) [20]); in addition, the band at 1210 cm^{-1} (ν(C=S) [20]) is weakened.

The spectra of the compounds $(R_nM)HTu$ (R = Me, Ph; $n = 1$ for M = Hg and $n = 2$ for M = Tl) show shifts with respect to the spectrum of H_2Tu that parallel those observed in HTuSMe, suggesting similar coordination in all of them, with the metal bound to the sulphur atom. The compound Me_2TlHTu, whose structure was reported previously [5], also has a linkage to N(1) and a weak interaction between the thallium atom and a C=O group from a neighbouring ligand molecule. The coordination of the N(1) atom appears to shift markedly the ring stretching modes initially located at 1445 and 1235 cm^{-1}.

Although the limitations on the use of ν(C=O) for diagnosing the coordinative mode for this type of ligand were pointed out above, we note that the position of this band in the spectra of the compounds PhHgHTu, Ph_2TlHTu and $Ph_2TlTuSMe$ is rather low, so the carbonyl group may be involved in the metal–ligand bond in these mononuclear derivatives.

On the other hand, there are also general trends in the spectra of the compounds $(R_nM)_2Tu$ and $R_nMTuSMe$ which suggest that the linkage of the ligand to the metal (or methyl) fragment is similar in all cases, the second R_nM group being bonded to N(3), as shown inequivocally the X-ray data for MeHgTuSMe.

(b) Organometal fragment and metal–ligand bond vibrations. The complexity of the ligand spectra in the regions where the bands associated with the organometallic fragment vibrations should appear make their assignment difficult in some cases. Thus in previously studied methylmercury compounds [22], $\delta_{sym}(CH_3)$ lies in the range 1170–1190 cm^{-1} a region where the ligand also shows some bands. It may thus be that the bands assigned to this mode in MeHgHTu (1150, 1160, and 1170 cm^{-1}, vide infra), $(MeHg)_2Tu$ (1190 and 1170 cm^{-1}), and MeHgTuSMe (1190 cm^{-1}) are not pure bands.

The compound MeHgHTu was previously prepared by Stocco et al. [4] who, on the basis of the complexity of the IR spectral region at about 500 cm^{-1}, postulated the occurrence of different ν(Hg–C) vibrations and suggested the presence of a mixture of *S*- and *N*-bonded isomers. This complexity was also observed for the product prepared by the authors, but not in any of the other compounds reported in this work.

Therefore this region in the IR and Raman spectra of the compounds obtained was analysed and the following bands were located: H_2Tu (545m, 525m(IR), 541m(R)), MeHgHTu (560m, 550m, 540m, 515s, 500s(IR), 550w, 530m–s(R)), $(MeHg)_2Tu$ (580s, 560w, 540m–s(IR), 563m, 539m–s(R)), PhHgHTu (580s, 540m(IR), 583m, 542w(R)), HTuSMe (580w, 560m, 530s(IR), 568m, 534m, 518w(R)). Note that: (i) the methylation of H_2Tu and its associated thione-thiol transition results in a greater separation in the IR spectrum of the α(ring) and δ(ring) bands [20] lying between 600 and 500 cm^{-1}, making one of them active in the Raman

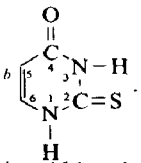
(continued on p. 30)

Table 9

^{1}H, ^{13}C and ^{199}Hg NMR parameters (in DMSO, δ en ppm from TMS [a] and J in Hz) for H_2Tu and HTuSMe complexes

Compound	NH	H(6)	H(5)	S-CH_3	MR_n	$^{3}J_{5,6}$	$^{n}J(^{1}H-M)$
H_2Tu [b]	12.36(b) [c](2) [d]	7.40(d)(1)	5.81(d)(1)			7.6	
HTuSMe	12.68(b)(1)	7.85(d)(1)	6.08(d)(1)	2,47(s)(3)		6.5	
MeHgHTu	12.45(b)(1)	7.56(d)(1)	5.94(d)(1)		0.72(t)(3)	6.6	191.7
PhHgHTu	12.54(b)(1)	7.62(d)(1)	5.99(d)(1)		7.45(H_o, dd)(2)	6.8	170.3
					7.33(H_m, t)(3)		
					7.22(H_p, tt)(1)		
Me_2TlHTu	11.61(b)(1)	7.42(d)(1)	5.71(d)(1)		0.84(d)(6)	6.7	421.4
Ph_2TlHTu	11.80(b)(1)	7.52(dd)(1)	5.81(dd)(1)		7.78(H_o, dd)(2)	6.9	451.6
					6.58(H_m, dt)(2)		131.0
MeHgTuSMe		7.86(d)(1)	6.08(d)(1)	2.55(s)(3)	0.85(t)(3)	6.3	207.3
PhHgTuSMe		7.88(dd)(1)	6.11(dd)(1)	2.54(s)(3)	7.48(H_o, dd)(2)	6.4	
					7.35(H_m, td)(2)		
					7.26(H_p, t)(1)		
$Ph_2TlTuSMe$		7.84(d)(1)	5.83(d)(1)	2.31(s)(3)	7.71(H_o, dd)(4)	6.0	454.2
					7.43(H_m, dt)(4)		138.4
					7.26(H_p, dt)(2)		50.0
$(MeHg)_2Tu$		7.63(d)(1)	6.11(d)(1)		0.77(t)(6)	6.5	195.5
$(PhHg)_2Tu$		7.68(d)(1)	6.15(d)(1)		7.47(H_o, dd)(2)	6.5	174.5
					7.33(H_m, td)(2)		
					7.24(H_p, tt)(1)		

	C(2)	C(4)	C(6)	C(5)	C(7)	MR_n	$^nJ(^{13}C-M)$	^{199}Hg	$W_{1/2}$ [e]
H_2Tu	176.3	171.3	142.3	105.4					
HTuSMe	163.6	163.0	153.7	109.7	12.8				
MeHgHTu		163.0	152.0(b)	109.5		7.8		−732.1	1400
PhHgHTu	169.3	163.0	152.5(b)	109.5		156.6(C_i)		−1072.7	1261
						137.0(C_o)	108.8		
						128.4(C_m)	183.5		
						128.0(C_p)			
Me_2TlHTu	176.8	163.1	150.8(b)	106.3		24.6	3003.5		
Ph_2TlHTu	176.3	163.1	150.6(b)	107.0		125.1–139.0			
MeHgTuSMe	166.2	166.6	153.7	110.6	13.5	1.5	1578.2	−918.1	71
PhHgTuSMe	166.5	166.4	153.8	110.4	13.7	148.6(C_i)		−1258.0	116
						137.3(C_o)	114.3(J_o)		
						128.5(C_m)	189.3(J_m)		
						128.5(C_p)			
$Ph_2TlTuSMe$	168.0	172.8	154.2	107.2	13.2	138.6–125.0			
$(MeHg)_2Tu$	172.9	166.3	153.2	109.5		4.6		−856.0	1290
$(PhHg)_2Tu$	173.9	165.9	151.7(b)	109.4		152.8(C_i)		−1185.8	3050
						137.3(C_o)	112.2		
						128.4(C_m)	187.7		
						128.1(C_p)			

[a] Except for ^{199}Hg, for which the values corresponding to the chemical shifts of ^{199}Hg are given in ppm and relative to $(CH_3)_2Hg$ neat. [b]  . [c] b = broad, d = doublet, m = multiplet, dd = doublet of doublets, t = triplet, tt = triplet of triplets. [d] Number of proton from integrated intensities. [e] Linewidth at half-height.

spectrum; (ii) the increased intensities observed in the Raman spectrum suggest that only the bands at 530 (MeHgHTu), and 563 and 539 cm^{-1} [$(MeHg)_2Tu$] have a definite ν(Hg–C) component, and in this last case are due to the *N*- and *S*-bonded MeHg groups. This leads us to suggest, as an possible alternative to the views of Stocco et al. [4], that the spectral complexity in this region (and also around 1170 cm^{-1} where the $\delta_{sym}(CH_3)$ mode is located) in the case of MeHgHTu may be due to the presence of S–Hg–CH_3 moieties situated in different surroundings in the solid state and experiencing different interactions with neighbouring molecules.

The ν_{asym}(C–Tl–C) (510 cm^{-1}) and ν_{sym}(C–Tl–C) (495 cm^{-1}) bands of the compound Me_2TlHTu are closer than those in other dimethylthallium systems [23], and the asymmetric stretching band is located in a lower energy region. This may be due to the unusual C–Tl–C bond angle for this thiouracil derivative [5].

Finally, in the compounds bearing the phenyl group, the *t* mode [24] that lies of about 250 cm^{-1} seems to be the "*X*-sensitive" mode most strongly affected by the metal coordination. All the compounds synthesized showed bands around this position and assignable to this mode although, particularly in the case of the HTuSMe complexes, these bands may have a ligand vibration component.

These mixing of vibrations will also normally take place between those of the ligand and the metal–ligand mode, and in view also of the complexity of the ligand spectra in the region between 600 and 100 cm^{-1}, no reliable assignation can be made for ν(M–L); however, by analogy with systems described elsewhere [22,24,25], the bands lying in the range 250–300 cm^{-1} and at about 200 cm^{-1} may include ν(M–S) and ν(M–N) components, respectively.

^1H, ^{13}C and ^{199}Hg NMR spectra

The compounds are water insoluble and scarcely soluble or insoluble in organic solvents except for DMSO and DMF, in which all were soluble. The most relevant spectral parameters of the ligands and the complexes are summarized in Table 9. The signals were assigned from the spectral data (position, multiplicity, integration) in the light of related information available [26].

Monometallated compounds. The ^{13}C NMR spectrum of MeHgHTu is very similar to that of the *S*-methylated ligand, which suggests that methylmercury(II) is coordinated to the sulphur atom of the deprotonated thiol form of 2-thiouracil. This hypothesis is supported by the coupling constant $^2J(^{199}Hg–^1H)$ of the ^1H NMR spectrum, as well as by the chemical shift of the mercury nucleus in the ^{199}Hg NMR spectrum [28].

The spectra of PhHgHTu are very similar to those of the methylated derivative, so that the conclusions about the coordination drawn in the previous paragraph can be extended to the phenylmercury-2-thiouracilate. It should be noted that $\delta(^{199}Hg)$ for this compound is further downfield than that for MeHgHTu, as is usually the case with the phenyl derivatives (see, for instance, the chemical shifts of $HgPh_2$ and $HgMe_2$ [27]).

The ^1H NMR spectra of MeHgHTu and PhHgHTu are fairly consistent with those obtained by Stocco et al. [4], except in respect of the signal due to the NH group, which was also observed for the phenylmercury(II) derivative under the experimental conditions used in the present work.

The reaction of RHg^+ with HTuSMe does not modify the signals from the ring protons, although it does affect those from C(2) and C(4). Both are deshielded in the

RHgTuSMe complexes, which is consistent with the binding of the organomercury ion to the N(3) atom of the ligand, as observed in the solid state for methylmercury(II)-2-*S*-methylthiouracilate.

The spectra of Me_2TlHTu are clearly different from those of the mercury derivatives of analogous composition. Thus, in the ^{13}C NMR spectrum, the C(2) signal lies very close to that observed for the free ligand or the N(1) methylated derivative [6]. As this signal is strongly influenced by the thione-thiol equilibrium (it shifts upfield with increasing prevalence of the thiol form [29]), we may conclude that its position in the spectrum of the dimethylthallium-2-thiouracilate reflects the retention in this compound of a high multiplicity in the carbon–sulphur linkage and, also possibly, the simultaneous coordination of the ligand via one of its ring nitrogens. Atom C(2) is clearly deshielded when the methylmercury(II) cation binds to the N(3) of the HTuSMe ligand (see Table 9).

The ^1H NMR spectrum of the dimethylthallium(III) complex also shows some effects which distinguish it from those of the above-mentioned mercury compounds. Thus the NH group is shielded by about 0.8 and 1.1 ppm with respect to those for MeHgHTu and HTuSMe, respectively. This is also observed for the diphenylthallium-2-thiouracilate. The positions of the signals of the other two ring protons are also different in the thallium complexes, H(5) being more shielded in the methylated derivative than in the free ligand.

For all the R_nMHTu compounds, the NMR spectra (and also the IR spectra registered in DMSO solution) show no evidence of hydroxylated forms.

The compound $Ph_2TlTuSMe$ also exhibits a different spectroscopic behaviour from that of the organomercury derivatives. The most salient differences in the ^{13}C NMR spectrum refer, in order of increasing magnitude significance, to carbons 2, 5 and 4. The most changed signal in the ^1H NMR spectrum is that from H(5), which is clearly shielded compared with that in the free ligand. The coupling constant $^3J_{5,6}$ is also slightly different. All this suggest the involvement of the oxygen atom in the coordination to the metal, probably together with N(3) atom.

Dimetallated complexes. The dimetallation shifts the ^{13}C NMR signal of C(4) downfield and, as in the case of the phenylmercury complexes (this signal could not be detected in the spectrum of the monometallated compound of methylmercury(II)) that of C(2) also, with respect to the monometallated compounds. The signal from C(6) is slightly deshielded in the case of $(MeHg)_2Tu$ and almost unchanged in the case of $(PhHg)_2Tu$. This suggests that the second organometallic cation, as $MeHg^+$ in MeHgTuSMe, is bonded to N(3). Comparison of the position of the ^{199}Hg NMR signals for these compounds and the monometallated complexes (Table 9) is very revealing in this respect. The signal of the dimetallated derivatives lies in an intermediate position between those for the RHgHTu (*S*-bonded) and RHgTuSMe (*N*-bonded) derivatives. This indicates that: (a) the organomercury fragment is rapidly exchanging its coordination position in the binuclear complexes; and (b) the chemical shift of the metal nucleus, as in the methylmercury(II) derivatives, is a good indicator of the type of atom which lies *trans* to the *R* group in the phenylmercury(II) derivatives.

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