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Monoorganomercury and diorganothallium derivatives of 2-thiobarbituric acid

María S. García Tasende *, Maria I. Suárez Gimeno, A. Sánchez, J.S. Casas * and J. Sordo

Departamento de Química Inorgánica, Universidad de Santiago de Compostela, 15706 Santiago de Compostela (La Coruña) (Spain)

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Abstract

Compounds of type $R_n MH_2Tb$ (R = Me, Ph; n = 1 (M = Hg), 2 (M = Tl), $H_3Tb = 2$ -thiobarbituric acid) have been prepared, and studied by vibrational (IR and Raman) and NMR (¹H, ¹³C, ¹⁹⁹Hg and ²⁰⁵Tl) spectroscopy. The organomercury derivatives have the metal bound to the deprotonated thiol sulphur atom of the ligand in both the solid state and in DMSO solution. The organothallium compounds, however, while having the metal bound to the sulphur atom and possibly to one of the nitrogen atoms of the ligand pyrimidine ring in the solid state, in DMSO form conducting solutions containing H_2Tb^- and R_2Tl^+ ions.

Introduction

Research on the interaction of the organometallic cations RHg^+ and R_2TI^+ with pyridine and pyrimidine bases undergoing thiol-thione tautomerism have begun to reveal significant differences in coordination between monoorganomercury and diorganothallium derivatives [1,2,3]. These differences can be expected to become more pronounced when the complexity of the ligand increases. To confirm this, we have investigated the interactions of methyl- and phenyl-mercury(II) and dimethyland diphenyl-thallium(III) with 2-thiobarbituric acid (H₁Tb).

Recent ¹³C NMR measurements in solution [4] have shown that the most important of the six neutral and three zwitterionic tautomers of H_3 Tb are:

^{*} Authors to whom correspondence should be addressed.



Forms II and III predominate, as expected, in solvents of large dielectric constant. Form II seems to be the most significant in the solid state [5]. Thus the ligand generated by deprotonation can potentially show a wide range of coordination modes. The results reported here show that, at least in solution, its coordination to RHg^+ cations differs widely from its coordination to R_2TI^+ . As far as we known, the only previous work in this particular field has consisted in partial analysis of the reactions of phenyl- and ethyl-mercury(II) with 5,5-dialkyl-2-thiobarbituric acid [6,7].

Experimental

(a) Reagents

Me₂TII and Ph₂TIBr were prepared as described elsewhere [8,9]. MeHgOOCCH₃, PhHgOOCCH₃, H₂TbSMe and H₃Tb were obtained commercially and used without further purification. Solvents were purified by standard methods. DMSO for conductivity measurements was purified [10] until a conductivity of ca. 10^{-7} ohm⁻¹ cm⁻¹ was reached.

(b) Synthesis of compounds

MeHgH₂Tb. 1.000 g (0.004 mol) of MeHgOOCCH₃ was added to 0.524 g (0.004 mol) of H₃Tb dissolved in 70 ml of methanol. Agitation and gentle heat for 24 h gradually produced a white precipitate which was filtered off and dried in vacuo (Found: C, 16.9; H, 1.7; N, 7.8. $C_5H_6HgN_2O_2S$ calcd.: C, 16.7; H, 1.7; N, 7.8%. M.p. 200 °C (decomposition). The main metallated ions (based on the isotope ²⁰²Hg) and base peak in the mass spectrum had m/z (%) = 359 (*M*, 17), 344 (*M* - Me, 1), 232 (Me₂Hg, 32), 202 (Hg, 17), 144 (L, 100), Molar conductivity in DMSO (10⁻³ *M* solution): 0.5 ohm⁻¹ cm² mol⁻¹.

PhHgH₂Tb. This was isolated as a white solid after a procedure similar to that used for MeHgH₂Tb (Found, C, 28.6; H, 2.0; N, 6.2. $C_{10}H_8HgN_2O_2S$ calcd.: C, 28.5; H, 1.9; N, 6.7%. M.p. 250 °C (decomposition). The main metallated ions in the mass spectrum (base peak, [Ph]) were at m/z (%) = 356 (Ph₂Hg, 15), 279 (PhHg, 9). Molar conductivity in DMSO ($10^{-3} M$ solution): 1.5 ohm⁻¹ cm² mol⁻¹).

Me₂TlH₂Tb. A solution of 0.003 mol of dimethylthallium(III) hydroxide (prepared as described previously [2]) in 75 ml of water was gradually added to 0.393 g (0.003 mol) of H₃Tb in 50 ml of methanol. The suspension was stirred for 2 h then the white solid was filtered off and dried in vacuo. (Found: C, 18.9; H, 2.4; N, 7.6. C₆H₉N₂O₂STl calcd.: C, 19.1; H, 2.4; N, 7.4%. M.p. 260 °C (decomposition). The main metallated ions in the mass spectrum (based on the isotope ²⁰⁵Tl) were at m/z(%) = 377 (M, 3), 363 (M – Me, 10), 348 (M – 2Me, 2), 235 (Me₂Tl, 51), 220 (MeTl, 18), 205 (Tl, 100). Molar conductivity in DMSO (10⁻³ M solution): 18 ohm⁻¹ cm² mol⁻¹). Ph₂TlH₂Tb. Prepared by a procedure similar to that used for Me₂TlH₂Tb. (Found, C, 37.9; H, 2.6; N, 7.6. $C_{16}H_{13}N_2O_2$ STl calcd.:, C, 38.4; H, 2.49; N, 7.6%. M.p. 260 °C (decomposition). No metallated peaks were observed in the mass spectrum. Molar conductivity in DMSO (10⁻³ *M* solution): 17 ohm⁻¹ cm² mol⁻¹).

(c) Chemical analysis and physical measurements

The C, H and N contents of the organomercury derivatives were determined by Galbraith Lab., Knoxville, TN, USA. The thallium compounds were analysed with a Perkin Elmer 240B elemental analyser. Conductivity measurements were made with a WTW conductivity meter. Mass spectra were obtained on a Kratos MS50TC spectrometer as described previously [2]. IR spectra were recorded with Nujol mulls, KBr pellets, or DMSO solutions on a Perkin Elmer 180 spectrometer. Raman spectra of powdered samples in capillary tubes were obtained on a Dilor Omars 89 spectrometer (Ar⁺ ion laser, 5145 Å), owing to fluorescence, only the spectra of Me₂TlH₂Tb and Ph₂TlH₂Tb could be obtained. ¹H, ¹³C and ¹⁹⁹Hg NMR spectra in either DMSO- d_6 or a DMSO- d_6 /DMSO mixture were recorded at room temperature on a Bruker WM-250 spectrometer at 250.13, 62.83 and 44.70 MHz, respectively; ¹H and ¹³C NMR shifts were measured relative to the solvent signal and ¹⁹⁹Hg shifts relative to external HgMe₂ (95%). ²⁰⁵Tl NMR spectra were recorded at room temperature on a Bruker AM-400 spectrometer, at 230.81 MHz and shifts are relative to external aqueous TICIO₄ after extrapolation to infinite dilution. Chemical shifts are given in ppm with positive values to high frequency. The ¹³C NMR spectrum of H_2Tb^- was recorded for a solution of the ligand in DMSO that had been partially neutralised by addition of an equivalent amount of NaOH in the same solvent.

Discussion

Table 1 shows the positions and assignments of the most important bands in the IR spectra of H_3 Tb [5] and its complexes. Data for H_2 TbSMe [11] are included for comparison. The IR spectrum of H_3 Tb reveals the presence of C=O, N-H and C-OH groups, showing that in the solid state the ligand is formed from the tautomeric forms proposed previously [5], although there are some intensity differences between our spectrum and those reported by Goel et al. [5].

Deprotonation and S-methylation of H_3 Tb shift some IR bands, but certain functional groups evidently remain. Comparison of the IR spectrum of H_2 TbSMe with data for 4,6-dimethyl-2-mercaptopyrimidine led Gupta et al. [11] to propose that the S-methylated derivative contains C=O, N-H and C-OH groups. On the other hand, the formation of the C-S-Me bond and the disappearance of the C=S group lead to the disappearance of the H_3 Tb band at 1165 cm⁻¹, which confirms the assignment of this band to the ν (C=S) mode [5].

Table 2 lists the most relevant ${}^{1}H$, ${}^{13}C$, ${}^{199}Hg$ and ${}^{205}Tl$ NMR data for the compounds in DMSO solution. The spectral parameters of the ligand are in good agreement with previous data [4,12].

Organomercury derivatives

The 1165 cm⁻¹ IR band is also absent from the spectra of the RHgH₂Tb compounds, suggesting the presence of an Hg-S bond. The remaining bands (Table

0				0	•			
H ₃ Tb	H ₂ TbSMe	MeHgH ₂ Tb	PhHgH ₂ Tb	Me ₂ TIH ₂ Tb		Ph ₂ TH ₂ Tb		Assignments
IR	IR	IR	IR	R	R	R	R	
3200w	3160w	3160sh	3100m	3160sh		3160sh	í	/(N-H)
3105m		3100тп		3100m		3100m		
		3060m	3065m	3060m	3084s	3060m	q	r(C ₅ −H)
1720m, 1650m	1650s	1650s	1650s	1640s		1630s		r(C4=0)
		1640s		1630s				
1625m	1620m	1610s	1620sh	1610s		1610sh		$v_{\rm ring} + \beta(\rm N-H)$
1570m	1580m	1595s	1600s	1590s		1580s		$v_{\text{ring}} + \beta(N-H)$
1540m		1550m	1540sh	1540m	1548s	1530m	1520s	$v_{\text{ning}} + \beta(N-H)$
	1500s, b	1500sh	1500m					
1380w	1380w	1395s	1380s	1390s		1410m		$\nu_{\rm ring}, \delta({\rm CH}_3)^{\ a}$
1355s	1350s	1370sh	1370sh	1370sh	1361m	1350m	1360m, b	Prine .
1290s	1270s	1310vs	1310vs	1310vs		1300vs		»(Č-OH)
1190w	1190s	1190s	1205w	1190s	1191vs	1190vs	1192m	β(C-H), β(C-OH) ^a
					1189m			
1165vs								v(C=S)
wv066	995s	1000m	1000m	1000m	1003m	1020m	1001	γ (C-H), ν_{ring}^{a} , β (N-H) a
	980m	960ms	960m	980m		1000m		ring i.p.b. "
	910w	910s	900m	920sh	931m	920m	930w	γ(C-H)
				900m		900m		
	870m	860m	860w	860w		860w		Gring
820vs	810vs	790vs	800vs	790vs		795m		γ(N-H)
				780s		780s		
	740m	730m	735s			720s		Ring breathing "
640w	630w	620 w	640sh	640w			647m	β (C=S), ν (C-S) ^a , γ (C ₅ -H) ^a
620w			620w	620w	616m	620w	617m	ring i.p.b.
525m	520m	525vs	525vs	530vs		530vs		β (C=O), ring i.p.b. ^a
490m	475m	490vs	490m	485vs	495vs	490vs		ring o.p.b.
^d Assignments spe	cific to H2TbSMe.	^b Not recorded.						

st significant bands in the IR and Raman spectra of H₃Tb, H₂TbSMe and H₃Tb comp

Table 1

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Compound C.1 C.31 T Model Mo	Commund	HN	HT JHJ	"`\ נ	н	HUS	aM		
H,Tb12.19b4.89b3.33b2.47H,FB/H,Tb11.3vb5.03s3.36b2.470.75191.7H,FB/H,Tb11.3vb5.03s3.36b7.40d170.2H,HF,Tb11.48vb5.03s3.04b1.7210.75191.7H,FF,Tb10.47b4.194.194.194.494.49H,FT,Tb10.47b4.194.194.194.49H,FT,Tb10.47b4.194.194.194.49H,FT,Tb10.47b4.194.194.194.49H,FT,Tb10.47b4.194.194.494.49H,TD10.47b10.47b4.194.494.49H,TD10.47b1.6116.258.214.194.49H,TD175.4b16.116.258.214.124.194.99H,TD175.4b16.116.258.214.124.134.60H,TD16.4116.258.214.124.134.66(1276)^4H,HH,TD16.45166.116.528.532.1234.66(1276)^4H,HH,TD166.1166.2166.3166.3166.3166.1H,HH,TD166.4166.3166.3166.3166.3166.1H,TD164.17.37.32.003.32.232.003.3H,HH,TD174.2164.17.937.1242.01.736/4H,HH,TD174.3166.1167.42.1232.003.3 <th>Numbrana</th> <th></th> <th>п-5-п</th> <th>Ĩ,</th> <th>F</th> <th>осп₃</th> <th>MK,</th> <th></th> <th></th>	Numbrana		п-5-п	Ĩ,	F	осп ₃	MK,		
H, Table 11340 315 247 05 1917 MeigH, To 11330 498 31360 05 1917 MeigH, To 11350 503 31360 05 1917 MeigH, To 113500 503 31360 05 105 1012 MeigH, To 1052a 408 605 605 408 607 102 MeigH, To 10.47b 405 4150 81 231 430 MeigH, To 10.47b 405 7214 336 436 MeigH, To 10.47b 166.1 162.5 82.1 177.1 430 H, Th 181.1b 175.4b 166.1 162.5 82.1 17.7 19.4 H, Th 181.1b 175.4b 166.1 162.5 82.1 17.1 H, Th 181.1b 175.4b 166.1 165.5 5.127 17.136 15.6 H, Th 181.5 166.1 165.2 <	н₃Ть	12.19b	4.89b	3.53b					
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	H ₂ TbSMe	11.54vb	5.15s			2.47			
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	MeHgH ₂ Tb	11.53vb	4.98s	3.36b	_		0.75		191.7
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Me ₂ TH ⁴ , Tb 1052s 408s He 7.77d 6.349 Pa, TH, Tb 10.47b 4.15b 1.415 8.07 He 7.77d 4.07 Pa, TH, Tb 10.47b 4.15b 1.640 7.17d 4.07 1.958 Ampound C_1 C_2 Cu, C_2 C_4 C_4 C_4 2.12 H, Th Me 181.1b 175.4b 166.1 162.5 8.21 1.27 1.91 2.01 3.16 H, Th Me Ist.1b 175.4b 166.1 8.53 1.27 9.1 -1.058.8(3.05) 4.66(1276) 2.18.1 MeHgH, Th 174.2 1.66.1 8.53 2.137.1 -1.058.8(3.05) 2.646(1276) 1.37.6 2.346.6(1276) 1.32.6 2.346.6(1276) 1.32.6 2.346.6(1276) 1.32.6 2.346.6(1276) 1.32.7 2.346.6(1276) 1.32.6 2.346.6(1276) 1.32.7 2.346.6(1276) 1.32.7 2.346.6(1276) 1.32.7 2.346.6(1276) 1.32.7 2.346.6(1276) 1.32.7 2.346.6(1276)							H ^m 7.	13t	
Me,THF,Th 10.23a 4.08s H 7.71d 4.49 Ph,TH,Th 10.47b 1.023a 4.08s H 7.71d 4.03 Ph,TH,Th 10.47b 1.053b 4.15b H 7.51d 1.96.7 4.03 H,Th 18.11b 175.4b 166.1 162.5 8.21 1.27 2.0 2.0 2.0 2.0 1.0 2.0 1.0 2.0 1.0 2.0 1.0 2.0 1.0 2.0 <t< td=""><th></th><td></td><td></td><td></td><td></td><td></td><td>H_p 7.2</td><td>Ĩ</td><td></td></t<>							H _p 7.2	Ĩ	
Ph_1TH+1D 10.47b 415b 415b 450.7 Ha 7.17d 450.7 Ph_1TH+1D 10.47b 415b 1154 150.1 139.8 450.7 139.8 Compound C2 C2 C4, C5 C3, (c5 C4, (c5 C3, (c5 C4, (c5 C4, (c5 C3, (c5 C4, (c5 C4	ϺͼͻͳͰͰϧͳϷ	10.52s	4.08s				0.87d		434.9
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$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$							H _p 7.3	2 dt	51.6
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$H_1^{T} P^-$ 176.1 164.0 76.1(?)* $H_1^{T} PSMe$ 163.7 167.4 85.7 12.7 $MeHgH_1^{T} P$ 166.8 166.1 85.3 12.7 $MeHgH_1^{T} P$ 166.6 166.1 85.3 12.7 $MeHgH_1^{T} P$ 166.6 166.1 85.3 0.1 -720.1 (376) d $MeHgH_1^{T} P$ 166.6 156.1 85.3 0.2 137.0 0.1 $Me_1^{T} H_1^{T} D$ 174.2 166.1 79.5 23.2 2909.3 346.6(1276) f $P_1^{T} H_2^{T} D$ 174.3 164.1 79.9 23.2 2909.3 2409.3 346.6(1276) f $P_1^{T} H_2^{T} D$ 174.3 164.1 79.9 23.2 2909.3 2409.3 7 $P_1^{T} H_2^{T} D$ 174.3 164.1 79.9 23.2 2909.3 246.6(1276) f $P_1^{T} H_2^{T} D$ 174.3 164.1 79.9 23.2 2909.3 246.6(1276) f $P_1^{T} H_2^{T} D$ 174.3 164.1 79.9 23.2 200.3.3 246.6(1276) f $P_1^{T} H_2^{T} $	H ₃ Tb	181.1b 175.4b	166.1 162.5	82.1					
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Phigh_iD 166.6 166.2 85.5 C, 158.0 - 1058.8(305)* Me_iTH_iD 174.2 166.9 79.5 C, 127.9 3446.6(1276)* Me_iTH_iD 174.2 166.1 79.5 23.2 2909.3 3446.6(1276)* Ph_iTH_iD 174.2 166.1 79.5 23.2 2909.3 3446.6(1276)* Ph_iTH_iD 174.3 164.1 79.9 138.5* 2909.3 3446.6(1276)* Ph_iTH_iD 174.3 164.1 79.9 138.5* 2909.3 3446.6(1276)* Ph_iDH_iD 174.3 164.1 79.9 138.5* 2909.3 3446.6(1276)* Phaite 174.3 164.1 79.9 132.7 132.7 288.4(2812)* Phaesof / in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublet, dt = doublet, dt = doublet of triplet, s = euadruplet. * Values of $W_{1/2}$ 125.1 125.1 * valuesof * for the breadth of the peak. * $d \ge 10^{-4}$ M solution. * 0.0104 M solution. * 0.011 M solution. * Assigned to the benzene ring signals	MeHgH,Tb	166.8	166.1	85.3		9.1		- 720.1 °(3	(و) م
Me_JTH_JTb174.2163.979.5Constraints ConstraintsConstraints ConstraintsConstraints Constraints3446.6(1276) f 23.2Ph_2TH_2Tb174.3164.179.923.22909.33446.6(1276) f 23.2Ph_2TH_2Tb174.3164.179.9138.5 f3446.6(1276) f 23.23446.6(1276) f 23.2Ph_2TH_2Tb174.3164.179.9138.5 f3446.6(1276) f 132.73446.6(1276) f 23.2Photes of J in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of the breacht of the peat. $d \approx 10^{-4} M$ solution. f 0.011 M solution. f Assigned to the benzene ring signals of $M_{1/2}$ of Ph_2TL.	PhHgH,Tb	166.6	166.2	85.5		C, 158.0		- 1058.8(30	5) *
Me_THH_Tb 174.2 163.9 79.5 C_{μ} 128.4 Ph_2TH_2Tb 174.3 163.9 79.5 23.2 2909.3 3446.6(1276) ^f Ph_2THH_2Tb 174.3 164.1 79.9 79.5 23.2 2909.3 3446.6(1276) ^f Ph_2THH_2Tb 174.3 164.1 79.9 138.5 ^g 2309.3 3446.6(1276) ^f Ph_2THH_2Tb 174.3 164.1 79.9 138.5 ^g 2388.4(2812) ^f Ph_2TH 132.7 132.71 132.71 132.71 238.5 a Values of <i>J</i> in Hz; b = broad, wb = very broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of $W_{1/2}$ in parentheses. ^c Accuracy poor due to the breadth of the peak. ^d = 10 ⁻⁴ M solution. ^f 0.0104 M solution. ^f 0.011 M solution. ^f Assigned to the benzene ring signals of Ph_2 TI.	•					C, 137.1			
Me_JTH_JD 174.2 163.9 79.5 C_127.9 3446.6(1276) f Ph_JTH_JD 174.3 164.1 79.9 138.5 g 2909.3 3446.6(1276) f Ph_JTH_JD 174.3 164.1 79.9 138.5 g 2909.3 3446.6(1276) f Ph_2TH_2Tb 174.3 164.1 79.9 138.5 g 2888.4(2812) f Nature 174.3 164.1 79.9 132.7 132.7 2888.4(2812) f a Values of <i>J</i> in Hz; b = broad, wb = very broad, s = singlet, d = doublet, dd = doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of $W_{1/2}$ in parentheses. ^f Accuracy poor due to the breadth of the peak. ^d = 10^{-4} M solution. ^f 0.0104 M solution. ^f 0.011 M solution. ^f Assigned to the benzene ring signals of Ph_2 TI.						C_ 128.4			
Me_THH_Tb 174.2 163.9 79.5 23.2 2909.3 $3446.6(1276)^{f}$ Ph_2THH_2Tb 174.3 164.1 79.9 138.5 s $348.4(2812)^{f}$ Ph_2THH_2Tb 174.3 164.1 79.9 132.7 232.7 $2888.4(2812)^{f}$ Ph_2THH_2Tb 174.3 164.1 79.9 132.7 132.7 $2888.4(2812)^{f}$ Pho2tecom $rage 132.7 129.1 122.1 122.1 122.1 a values of J in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. b Values of W_{1/2} in parentheses. c Accuracy poor due to the breadth of the peak. d \approx 10^{-4} M solution. f 0.011 M solution. f Assigned to the benzene ring signals of Ph_2TI. $						C, 127.9			
Ph_2TH_2Tb 174.3164.179.9138.5 s2388.4(2812) / Ph_2TH_2Tb 132.7132.7129.1 129.1 129.1129.1 $n_2 = broad$, vb = very broad, s = singlet, d = doublet of doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of $W_{1/2}$ in parentheses. ^c Accuracy poor due to the breadth of the peak. ^d = 10^{-4} M solution. ^c 0.0104 M solution. ^f 0.011 M solution. ^f Assigned to the benzene ring signals of Ph_2T1 .	Me,TIH,Tb	174.2	163.9	79.5		23.2	2909.3		3446.6(1276) ^f
132.7 129.1 129.1 125.1 in parentheses. ⁶ Accuracy poor due to the breadth of the peak. ^d $\approx 10^{-4}$ M solution. ⁶ 0.010 M solution. ^f 0.011 M solution. ^f Assigned to the benzene ring signals of Ph_2TI .	Ph,TH,Tb	174.3	164.1	79.9		138.5 #			2888.4(2812)
129.1 ^a Values of J in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of $W_{1/2}$ in parentheses. ^c Accuracy poor due to the breadth of the peak. ^d $\approx 10^{-4} M$ solution. ^d 0.0104 M solution. ^f 0.011 M solution. ^f Assigned to the benzene ring signals of Ph_2^{-1} .	•					132.7			~
^a Values of J in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of $W_{1/2}$ in parentheses. ^c Accuracy poor due to the breadth of the peak. ^d $\approx 10^{-4}$ M solution. ^e 0.0104 M solution. ^f 0.011 M solution. ^g Assigned to the benzene ring signals of Ph_2 TI.						129.1			
^a Values of J in Hz; b = broad, vb = very broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, dt = doublet of triplets, c = cuadruplet. ^b Values of W _{1/2} in parentheses. ^c Accuracy poor due to the breadth of the peak. ^d = 10 ⁻⁴ M solution. ^e 0.0104 M solution. ^f 0.011 M solution. ^g Assigned to the benzene ring signals of Ph ₂ TI.						125.1			
values of J in ris, $v = vroad$, $v = very broad$, $s = singlet$, $d = doubted$, $du = doubted$, $u = upted$, $dt = doubted$ of inplet, $dt = doubted$, $u = u = doubted$, $u = u = doubted$, $u = doubt$	0 1/-1	- 11 t - t t	- Landa	- be veldand	dention of d		inter de destruction		
	Values of J L	D HZ ; $\mathbf{D} = \mathbf{D} \mathbf{D} \mathbf{a} \mathbf{a}$, $\mathbf{v} \mathbf{b} = \mathbf{v} \mathbf{c}$. Area racy poor due to	ify Droad, s = singict, u : the breadth of the neak	$= \text{doublet, du} = \frac{d}{d} = 10^{-4} M_{\odot}$	doublet of t	Joublets, t = tr 0104 M soluti	ipiet, at = aoubie ion ⁷ 0.011 M sol	t of tripicts, c = ntion. ⁶ Assign	= cuadruplet. Values of $w_{1/2}$
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	of Fm_2^{11} .								

, F į 205 TT 1140 ¹H ¹³C ¹⁹⁹H₆

Table 2

1) have a pattern similar to that for H_2 TbSMe, indicating that the ligand rearranges in a similar way in the S-methylated derivative and the organomercury compounds.

With regard to the organometallic fragment modes in the MeHg compound, $\delta_{sym}(CH_3)$, $\rho(CH_3)$ and $\nu(Hg-C)$ strengthen the ligand bands located at 1190, 790, and 525 cm⁻¹ respectively, while the X-sensitive t mode in the PhHg derivative is located at 240 cm⁻¹ [13].



Fig. 1. (a) ¹H NMR spectrum of MeHgH₂Tb in DMSO-d₆, (b) The spectrum after addition of a few drops of D_2O .

The ¹³C NMR signals for RHgH₂Tb and H₂TbSMe are similar (Table 2), showing that in the mercury complexes the ligand adopts a thiol form. Furthermore, the signals associated with C₂ are shielded in RHgH₂Tb with respect to that for H₃Tb, which is normal when this type of ligand changes from thione to thiol [2]. The ²J(¹⁹⁹Hg⁻¹H) value and the ¹⁹⁹Hg chemical shift of MeHgH₂Tb, which is very similar to that observed in (8-mercaptoguaninate)methylmercury(II), a complex containing an Hg-S bond [14], both suggest that the mercury atom is bound to a deprotonated sulphydryl group. With regard to the other groups involved in the tautomers of the free ligand: (i) the C₅ signals correspond to a vinyl carbon [4]; (ii) the ¹H NMR spectra show signals for N-H groups; and (iii) although the presence of DHO species in the solvent prevents confirmation of the presence or absence of OH groups in RHgH₂Tb, their presence is suggested by broad bands located at approximately 3400 cm⁻¹ in the IR spectra of solutions in DMSO.

The above results mean that, in $DMSO-d_6$ solutions as in the solid state, the thiobarbiturates of the monoorganomercury cations studied, preferentially, adopt the form



although the presence of the corresponding zwitterion and/or small concentrations of other forms cannot be ruled out. That the ligand protons remain mobile after complexation can be seen by comparing the spectra of the methylmercury(II) derivative in DMSO- d_6 solution before and after addition of a few drops of D₂O (Fig. 1).

Organothallium derivatives

The IR spectra of the thallium compounds exhibit no band corresponding to the $H_3Tb \nu$ (C=S) mode, implying, as for RHgH₂Tb, that the S atom is involved in coordination to the metal. The locations of the bands for the C=O, N-H and C-OH groups (Table 1) suggest their status to be similar to that suggested for the RHg⁺ complexes. Certain features, such as the absence of ν_{ring} at 1500 cm⁻¹, the splitting of γ (C-H) and γ (N-H) modes and the lack of ring breathing in Me₂TlH₂Tb, nevertheless suggest that, as in similar systems [3], the N atom also takes part in coordination to the metal. The Raman spectra, despite their poor quality, confirm the presence of the C₅-H group [11], and so rule out the existence of the ligand Form I in the thallium compounds.

With regard to the vibrations of the organometallic fragment, in Me₂TlH₂Tb the $\delta_{sym}(CH_3)$ and $\rho(CH_3)$ modes strengthen the ligand bands located at 1190 and 790 cm⁻¹; $\nu_{asym}(C-TI-C)$ is located at 530 cm⁻¹; and $\nu_{sym}(C-TI-C)$ occurs as an intense Raman band at 495 cm⁻¹.

In DMSO solution, the R_2TIH_2Tb complexes produce species which seem to differ both from those formed from RHgH₂Tb and from that suggested for the solid state. The NMR data (Table 2) show that in the thallium complexes the C_2 signal is shielded much less than in RHgH₂Tb, so that the ligand part of the R_2TIH_2Tb spectra is very similar to that in the spectrum of the H_2Tb^- ion, which in aqueous solution takes the following form [15]:



The spectral parameters of the organometallic fragments likewise suggest that the dissolved species are ionic in nature. The ${}^{1}J({}^{205}Tl-{}^{13}C)$ coupling constant for Me₂TlH₂Tb is similar to that for Me₂TlNO₃ in the same solvent at a similar concentration [16] and the values of ${}^{2}J({}^{205}Tl-{}^{1}H)$ and the ${}^{205}Tl$ chemical shift are both close to those for dimethylthallium(III) perchlorate and nitrate in DMSO [16]. It therefore seems justifiable to represent solutions of these complexes in DMSO as a mixture of solvated R₂Tl⁺ and H₂Tb⁻ ions in equilibrium with a small proportion of undissociated species. This conclusion is supported by the molar conductivity measurements in DMSO (see Experimental part). R₂TlH₂Tb shows conductivities close to that for a 1/1 electrolyte (23-42 ohm⁻¹ cm² mol⁻¹ (10)), whereas the values for RHgH₂Tb indicate that ions are not formed.

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