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Monoorganomercury and diorganothallium derivatives of 2-thiobarbituric acid

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Abstract

Compounds of type R_nMH_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, ^{13}C, ^{199}Hg and ^{205}Tl) 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_2Tl^+ 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 dimethyl- and diphenyl-thallium(III) with 2-thiobarbituric acid (H_3Tb).

Recent ^{13}C NMR measurements in solution [4] have shown that the most important of the six neutral and three zwitterionic tautomers of H_3Tb are:

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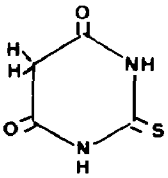

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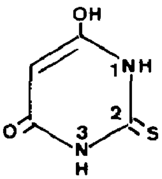

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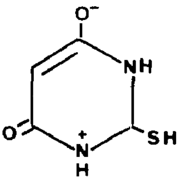

III

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_2Tl^+. 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

Me_2TlI and Ph_2TlBr were prepared as described elsewhere [8,9]. $MeHgOOCCH_3$, $PhHgOOCCH_3$, H_2TbSMe and H_3Tb 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

$MeHgH_2Tb$. 1.000 g (0.004 mol) of $MeHgOOCCH_3$ was added to 0.524 g (0.004 mol) of H_3Tb 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 ^{202}Hg) and base peak in the mass spectrum had m/z (%) = 359 (M, 17), 344 (M – Me, 1), 232 (Me_2Hg, 32), 202 (Hg, 17), 144 (L, 100), Molar conductivity in DMSO (10^{-3} M solution): 0.5 ohm^{-1} cm^2 mol^{-1}.

$PhHgH_2Tb$. This was isolated as a white solid after a procedure similar to that used for $MeHgH_2Tb$ (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 (Ph_2Hg, 15), 279 (PhHg, 9). Molar conductivity in DMSO (10^{-3} M solution): 1.5 ohm^{-1} cm^2 mol^{-1}).

Me_2TlH_2Tb. 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 H_3Tb 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. $C_6H_9N_2O_2STl$ 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 ^{205}Tl) were at m/z (%) = 377 (M, 3), 363 (M – Me, 10), 348 (M – 2Me, 2), 235 (Me_2Tl, 51), 220 (MeTl, 18), 205 (Tl, 100). Molar conductivity in DMSO (10^{-3} M solution): 18 ohm^{-1} cm^2 mol^{-1}).

Ph_2TlH_2Tb. Prepared by a procedure similar to that used for Me_2TlH_2Tb. (Found, C, 37.9; H, 2.6; N, 7.6. $C_{16}H_{13}N_2O_2STl$ 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} cm^2 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 Me_2TlH_2Tb and Ph_2TlH_2Tb could be obtained. ^1H, ^{13}C and ^{199}Hg 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 ^{13}C NMR shifts were measured relative to the solvent signal and ^{199}Hg shifts relative to external $HgMe_2$ (95%). ^{205}Tl NMR spectra were recorded at room temperature on a Bruker AM-400 spectrometer, at 230.81 MHz and shifts are relative to external aqueous $TlClO_4$ after extrapolation to infinite dilution. Chemical shifts are given in ppm with positive values to high frequency. The ^{13}C 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_3Tb [5] and its complexes. Data for H_2TbSMe [11] are included for comparison. The IR spectrum of H_3Tb 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_3Tb shift some IR bands, but certain functional groups evidently remain. Comparison of the IR spectrum of H_2TbSMe 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_3Tb 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 ^1H, ^{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 $RHgH_2Tb$ compounds, suggesting the presence of an Hg–S bond. The remaining bands (Table

Table 1

Most significant bands in the IR and Raman spectra of H_3Tb, H_2TbSMe and H_3Tb complexes

H_3Tb	H_2TbSMe	$MeHgH_2Tb$	$PhHgH_2Tb$	Me_2TlH_2Tb		Ph_2TlH_2Tb		Assignments
IR	IR	IR	IR	IR	R	IR	R	
3200w	3160w	3160sh	3100m	3160sh		3160sh		ν(N–H)
3105m		3100m		3100m		3100m		
		3060m	3065m	3060m	3084s	3060m	[b]	$\nu(C_5{-}H)$
1720m, 1650m	1650s	1650s	1650s	1640s		1630s		$\nu(C_4{=}O)$
		1640s		1630s				
1625m	1620m	1610s	1620sh	1610s		1610sh		ν_{ring} + β(N–H)
1570m	1580m	1595s	1600s	1590s		1580s		ν_{ring} + β(N–H)
1540m		1550m	1540sh	1540m	1548s	1530m	1520s	ν_{ring} + β(N–H)
	1500s, b	1500sh	1500m					ν_{ring} [a]
1380w	1380w	1395s	1380s	1390s		1410m		ν_{ring}, $\delta(CH_3)$ [a]
1355s	1350s	1370sh	1370sh	1370sh	1361m	1350m	1360m, b	ν_{ring}
1290s	1270s	1310vs	1310vs	1310vs		1300vs		ν(C–OH)
1190w	1190s	1190s	1205w	1190s	1191vs 1189m	1190vs	1192m	β(C–H), β(C–OH) [a]
1165vs								ν(C=S)
990vw	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. [a]
	910w	910s	900m	920sh	931m	920m	930w	γ(C–H)
				900m		900m		
	870m	860m	860w	860w		860w		α_{ring}
820vs	810vs	790vs	800vs	790vs		795m		γ(N–H)
				780s		780s		
	740m	730m	735s			720s		Ring breathing [a]
640w	630w	620w	640sh	640w			647m	β(C=S), ν(C–S) [a], $\gamma(C_5{-}H)$ [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.

[a] Assignments specific to H_2TbSMe. [b] Not recorded.

Table 2

^1H, ^{13}C, ^{199}Hg and ^{205}Tl NMR parameters for H_3Tb complexes [a,b]

Compound	NH	$C{=}C_5\text{-}H$	$C_5{<}{}^{H}_{H}$	SCH_3	MR_n	$^nJ(^1H\text{-}M)$
H_3Tb	12.19b	4.89b	3.53b			
H_2TbSMe	11.54vb	5.15s		2.47		
$MeHgH_2Tb$	11.53vb	4.98s	3.36b		0.75	191.7
$PhHgH_2Tb$	11.48vb	5.03s			H_o 7.49dd H_m 7.33t H_p 7.23t	170.2
Me_2TlH_2Tb	10.52s	4.08s			0.87d	434.9
Ph_2TlH_2Tb	10.47b	4.15b			H_o 7.77d H_m 7.51dt H_p 7.32 dt	450.7 139.8 51.6

Compound	C_2	C_2'	C_4, C_6	C_4', C_6'	$C_5(=)$	SCH_3	MR_n	$^nJ(^{13}C\text{-}M)$	^{199}Hg	^{205}Tl
H_3Tb	181.1b	175.4b	166.1	162.5	82.1					
H_2Tb^-	176.1		164.0		76.1(?) [c]					
H_2TbSMe	163.7		167.4		85.7	12.7				
$MeHgH_2Tb$	166.8		166.1		85.3		9.1		-720.1 [c](376) [d]	
$PhHgH_2Tb$	166.6		166.2		85.5		C_i 158.0 C_o 137.1 C_m 128.4 C_p 127.9		-1058.8(305) [e]	
Me_2TlH_2Tb	174.2		163.9		79.5		23.2	2909.3		3446.6(1276) [f]
Ph_2TlH_2Tb	174.3		164.1		79.9		138.5 [g] 132.7 129.1 125.1			2888.4(2812) [f]

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[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_2Tl.

1) have a pattern similar to that for H_2TbSMe, 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 ν(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].

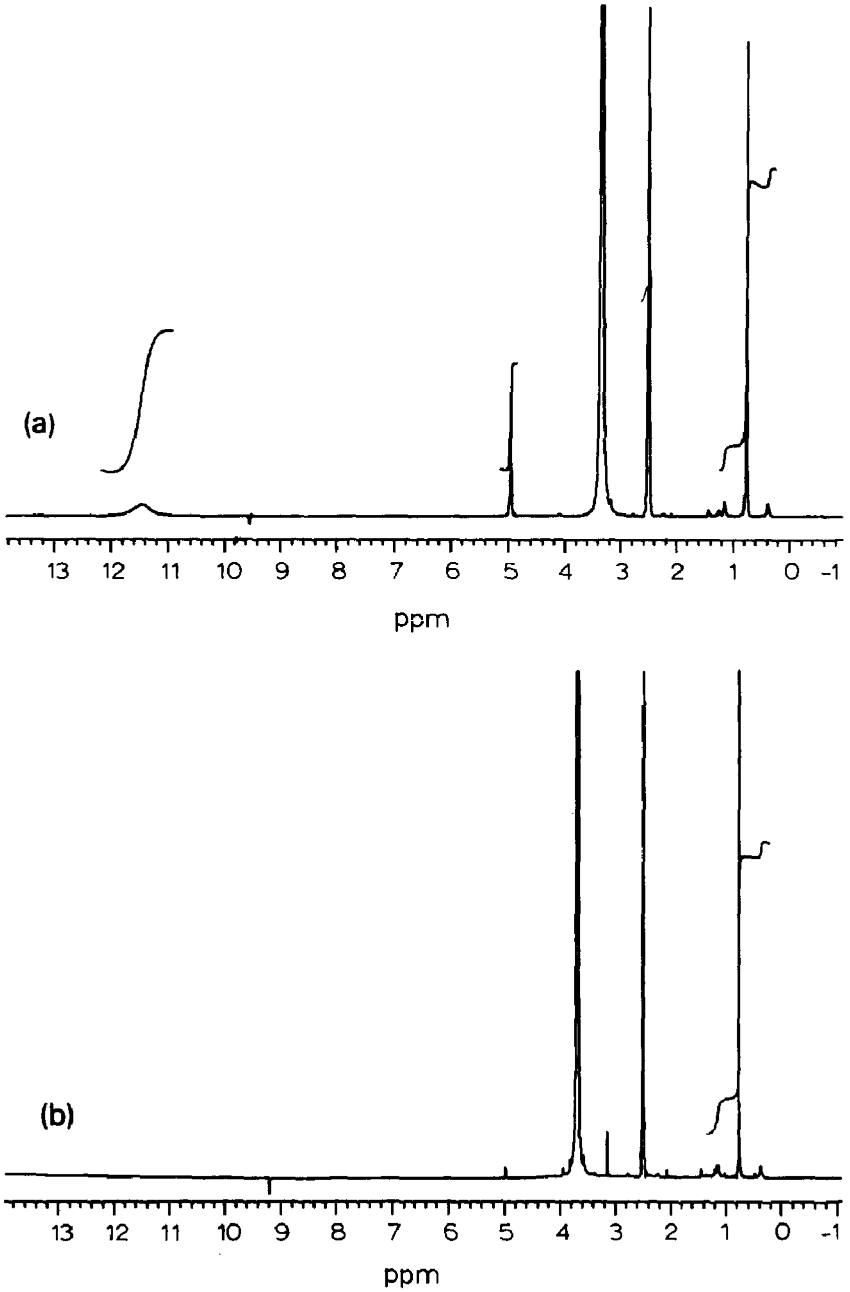
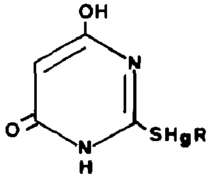


Fig. 1. (a) ^{1}H NMR spectrum of MeHgH$_2$Tb in DMSO-d$_6$, (b) The spectrum after addition of a few drops of D_2O.

The ^{13}C NMR signals for $RHgH_2Tb$ and H_2TbSMe are similar (Table 2), showing that in the mercury complexes the ligand adopts a thiol form. Furthermore, the signals associated with C_2 are shielded in $RHgH_2Tb$ with respect to that for H_3Tb, which is normal when this type of ligand changes from thione to thiol [2]. The $^2J(^{199}Hg-^1H)$ value and the ^{199}Hg chemical shift of $MeHgH_2Tb$, 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 C_5 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 $RHgH_2Tb$, 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



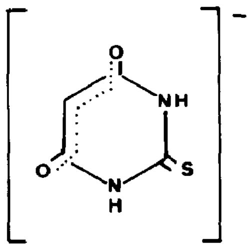
although the presence of the corresponding zwitterion and/or small concentrations of other forms cannot be ruled out. That the ligand protons remain mobile after complexation can be seen by comparing the spectra of the methylmercury(II) derivative in DMSO-d_6 solution before and after addition of a few drops of D_2O (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 $RHgH_2Tb$, 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 Me_2TlH_2Tb, 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 C_5–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 Me_2TlH_2Tb the $\delta_{sym}(CH_3)$ and $\rho(CH_3)$ modes strengthen the ligand bands located at 1190 and 790 cm^{-1}; ν_{asym}(C–Tl–C) is located at 530 cm^{-1}; and ν_{sym}(C–Tl–C) occurs as an intense Raman band at 495 cm^{-1}.

In DMSO solution, the R_2TlH_2Tb complexes produce species which seem to differ both from those formed from $RHgH_2Tb$ 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 $RHgH_2Tb$, so that the ligand part of the R_2TlH_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 $^{1}J(^{205}\text{Tl}-^{13}\text{C})$ coupling constant for $\text{Me}_2\text{TlH}_2\text{Tb}$ is similar to that for Me_2TlNO_3 in the same solvent at a similar concentration [16] and the values of $^{2}J(^{205}\text{Tl}-^{1}\text{H})$ 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 R_2Tl^+ and H_2Tb^- ions in equilibrium with a small proportion of undissociated species. This conclusion is supported by the molar conductivity measurements in DMSO (see Experimental part). $\text{R}_2\text{TlH}_2\text{Tb}$ shows conductivities close to that for a 1/1 electrolyte (23–42 ohm^{-1} cm^2 mol^{-1} (10)), whereas the values for RHgH_2Tb indicate that ions are not formed.

Acknowledgements

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