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Synthesis, and spectral and X-ray characterization, of methylmercury(II) and dimethylthallium(III) complexes of 2-furanthiocarboxyhydrazide

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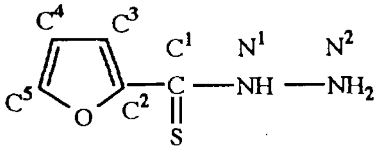
Abstract

Reaction of an ethanolic solution of 2-furanthiocarboxyhydrazide (Hfth) with an aqueous solution of methylmercury(II) or dimethylthallium(III) hydroxides yielded HgMefth and $TlMe_2fth$, respectively. The thallium compound crystallizes in the $P2_1/n$ space group (No. 14) with $a=7.392(4)$, $b=23.612(3)$, $c=11.865(4)$ Å, $\beta=101.36(2)°$ and $Z=8$. There are two different thallium atoms in each asymmetric unit (Tl(1) and Tl(2)). Tl(1) is bound to its two methyl groups, and an N(2),S-chelate ligand. Tl(2) is coordinated to its methyl groups, and to two ligands, one via S and another via N(1). Both thallium atoms have weak additional interactions, those of Tl(2) involving the O atoms of furan rings. The IR spectrum of HgMefth suggest that its ligand is S-bonded, although a weak N(1)–Hg interaction cannot be ruled out. The ^{1}H, ^{13}C and ^{199}Hg or ^{205}Tl NMR behaviour of the complexes in DMSO is also discussed.

Introduction

The methylmercury(II) and dimethylthallium(III) derivatives of cyclopentanone thiosemicarbazone have rather similar ligand bonding schemes [1, 2] in spite of the two organometallic cations usually differing in their coordination chemistry. Deprotonated thiosemicarbazones can coordinate through their sulphur and imine nitrogen atoms to form stable five-membered rings with the metal. Like thiosemicarbazones, thiohydrazides [3] contain –N(H)–C(=S)– groups but deprotonated thiohydrazides only form chelate rings via their $-NH_2$ group. Since the affinity of $MeHg^+$ for deprotonated N–H groups can be expected to be very different from its affinity for amino groups and this difference may be less for $TlMe_2^+$, we suspected that methylmercury(II) and dimethylthallium(III) would not exhibit similar ligand coordination in thiocarboxyhydrazidates as they do in thiosemicarbazonates. This suspicion was confirmed by the work described in this article, in which we synthesized and characterized the ligand coordination of the compounds HgMefth and $TlMe_2fth$, where Hfth is 2-furanthiocarboxyhydrazide.



Experimental

Preparation of the compounds

The ligand, 2-furanthiocarboxyhydrazide (Hfth), was synthesized using procedures described earlier [4, 5].

$TlMe_2fth$

To an aqueous solution of $TlMe_2OH$ (3.1 mmol) prepared as described previously [6] was added, dropwise, an ethanolic solution of Hfth (0.44 g, 3.1 mmol). The mixture was stirred for 1 h, and the crystalline precipitate formed was filtered off and vacuum dried. m.p. 158 °C. *Anal.* Found: C, 22.1; H, 2.9; N, 7.5. Calc. for $C_7H_{11}N_2OSTl$: C, 22.4; H, 2.9; N, 7.5%. In the mass spectrum, the base peak and the main metallated ions (based on the isotope ^{205}Tl) had m/z (%) = 439

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($C_7H_{14}N_4OS_2Tl$, 3), 424 ($C_6H_{11}N_4OS_2Tl$, 2), 218 ($C_6H_{10}N_4OS_2$, 100). $\Lambda_M = 20.43$ ohm^{-1} cm^2 mol^{-1}.

HgMefth

An aqueous solution of HgMeOH, prepared by reacting 0.88 g (3.5 mmol) of HgMeCl (Ventron) with excess Ag_2O, was added to a solution of Hfth (0.50 g, 3.5 mmol) in ethanol. The mixture was kept stirring overnight and the yellow solid formed was filtered out, washed with water and ethanol, and vacuum dried. m.p. 78 °C. *Anal.* Found: C, 20.7; H, 1.7; N, 7.4. Calc. for $C_6H_8N_2OSHg$: C, 20.1; H, 2.2; N, 7.8%. In the mass spectrum, the base peak and the main metallated ions (based on the isotope ^{202}Hg) had m/z (%) = 464 ($C_2H_6SHg_2$, 3), 449 (CH_3SHg_2, 2), 358 (M, 26), 249 (CH_3SHg, 3), 217 (CH_3Hg, 10), 202 (Hg, 7), 142 ($C_5H_6N_2OS$ (Hfth), 18), 111 (C_5H_3OS, 100). $\Lambda_M = 1.13$ ohm^{-1} cm^2 mol^{-1}.

Measurements

Elemental analyses (C, H and N) were performed in Perkin-Elmer 240B and Carlo-Erba 1108 elemental analysers. Conductivity measurements in DMSO ($c = 10^{-3}$ M) were made using a WTW conductivity meter. IR spectra were recorded in KBr pellets on a Perkin-Elmer 1330 spectrometer. The mass spectra were obtained using a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (70 eV). All the ions were identified using DS90 software. ^1H (250.13 MHz), ^{13}C (62.83 MHz) and ^{199}Hg (44.80 MHz) spectra were recorded at room temperature in DMSO-d_6 on a Bruker WM 250 spectrometer. ^{205}Tl (230.81 MHz) spectra were recorded at room temperature in DMSO on a Bruker AM 400 spectrometer.

Crystal structure determination

Crystal data

$C_7H_{11}N_2OSTl$, monoclinic, space group $P2_1/n$ (derived from $P2_1/c$, No. 14) $a = 7.392(4)$, $b = 23.612(3)$, $c = 11.865(4)$ Å, $\beta = 101.36(2)°$, $V = 2030.2$ Å^3, $Z = 8$, $D_x = 2.458$ g cm^{-3}, $\mu = 162.31$ cm^{-1}, $F(000) = 1376$ and $T = 293$ K.

Data collection and processing

A colourless prismatic crystal was examined at room temperature on an Enraf-Nonius CAD4 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation. Cell parameters were determined by least-squares on setting angles from 25 reflections. Intensity data in the range $3 < \theta < 24$ were collected by the ω–2θ scan mode (scan width $[0.80 + 0.35 \tan(\theta)]$, max speed 5.0 min^{-1}); *hkl* range: $h < 9$, $k < 28$, $-14 < l < 14$. Of the 3552 reflections measured, 3281 were unique ($R_{int} = 0.066$) and 1897 observed with $I > 3\sigma(I)$ were used in refinement after correction for Lorentz and polarization effects and application of an empirical correction factor [7] (minimum and maximum transmission values 0.459, 1.727).

Structure analysis and refinement

The structure was solved by the heavy atom method. After locating the Tl atom with a Patterson map, subsequent full-matrix least-squares refinement and interpretation of Fourier difference maps enabled all the non-hydrogen atoms in the structure to be located. Only Tl and S atoms were anisotropic. Hydrogen atoms were not found in the difference maps and their positions were not calculated. Function minimized: $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$. 113 parameters refined. Inspection of F_c and F_o values indicated the need for a correction for secondary extinction $[F_{corr} = F_c (1 + kF^2/\sin 2\theta')^{0.25}]$ where k refined to 3.3617×10^{-8} in the final run; excluded unobserved reflections $R = 0.0409$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.056$; max. shift/e.s.d. in the final least-squares cycle 0.01. Refinement of data included scattering factors and corrections for anomalous dispersion from ref. 8. Calculations were performed on a Dec Micro VAX II computer using the program SHELX86 [9] and SDP/VAX [10]. Atomic positions, bond lengths and angles are listed in Tables 1, 2 and 3, respectively.

TABLE 1. Positional parameters and their e.s.d.s for $TlMe_2fth$

Atom	*x*	*y*	*z*
Tl(1)	0.1479(1)	0.08449(4)	0.43420(8)
Tl(2)	0.5565(1)	0.17271(4)	0.82082(8)
S(1)	0.2440(8)	−0.0090(3)	0.5878(5)
S(2)	1.0882(8)	0.2713(3)	1.1146(5)
O(1)	0.392(2)	0.0666(8)	0.896(1)
O(2)	0.588(3)	0.2056(9)	1.093(2)
N(1)	0.438(3)	0.0835(8)	0.678(2)
N(2)	0.468(3)	0.0925(8)	0.568(2)
N(3)	0.774(3)	0.2613(9)	0.954(2)
N(4)	0.851(3)	0.3001(9)	0.888(2)
C(1)	0.337(3)	0.038(1)	0.696(2)
C(2)	0.310(3)	0.030(1)	0.812(2)
C(3)	0.215(4)	−0.009(1)	0.858(2)
C(4)	0.233(4)	0.003(1)	0.979(2)
C(5)	0.346(4)	0.049(1)	0.995(2)
C(6)	0.236(3)	0.049(1)	0.287(2)
C(7)	0.505(4)	0.365(1)	0.043(2)
C(8)	0.865(3)	0.2488(9)	1.056(2)
C(9)	0.772(3)	0.210(1)	1.117(2)
C(10)	0.837(3)	0.174(1)	1.207(2)
C(11)	0.684(4)	0.148(1)	1.238(3)
C(12)	0.534(4)	0.167(1)	1.170(2)
C(13)	0.788(3)	0.300(1)	0.343(2)
C(14)	0.334(4)	0.366(1)	0.342(2)

TABLE 2. Bond distances (Å) in $TlMe_2fth$ and their e.s.d.s

Tl(1)–S(1)	2.862(2)	O(2)–C(12)	1.42(1)
Tl(1)–N(2)	2.586(7)	N(1)–N(2)	1.384(9)
Tl(1)–C(6)	2.16(1)	N(1)–C(1)	1.34(2)
Tl(1)–C(7)	2.18(2)	N(3)–N(4)	1.40(2)
Tl(2)–S(2)	2.831(2)	N(3)–C(8)	1.30(2)
Tl(2)–N(1)	2.734(7)	C(1)–C(2)	1.44(1)
Tl(2)–C(13)	2.156(9)	C(2)–C(3)	1.33(1)
Tl(2)–C(14)	2.22(1)	C(3)–C(4)	1.43(1)
S(1)–C(1)	1.738(8)	C(4)–C(5)	1.37(1)
S(2)–C(8)	1.741(8)	C(8)–C(9)	1.43(1)
O(1)–C(2)	1.37(2)	C(9)–C(10)	1.37(1)
O(1)–C(5)	1.36(1)	C(10)–C(11)	1.40(1)
O(2)–C(9)	1.35(2)	C(11)–C(12)	1.31(1)
Tl(1)···S(1″)	3.367(2)	Tl(2)···O(1)	2.994(6)
Tl(1)···N(4′)	3.210(8)	Tl(2)···O(2)	3.279(7)

TABLE 3. Bond angles (°) in $TlMe_2fth$ and their e.s.d.s

S(1)–Tl(1)–N(2)	65.4(2)	S(1)–C(1)–C(2)	120.4(7)
S(1)–Tl(1)–C(7)	97.4(3)	N(1)–C(1)–C(2)	116.7(7)
S(1)–Tl(1)–C(7)	97.4(3)	O(1)–C(2)–C(1)	118.4(8)
N(2)–Tl(1)–C(6)	98.1(3)	O(1)–C(2)–C(3)	109.2(8)
N(2)–Tl(1)–C(7)	94.9(4)	C(1)–C(2)–C(3)	132.5(9)
C(6)–Tl(1)–C(7)	163.0(4)	C(2)–C(3)–C(4)	109.1(9)
S(2)–Tl(2)–N(1)	84.1(2)	C(3)–C(4)–C(5)	103.5(9)
S(2)–Tl(2)–C(13)	101.5(2)	O(1)–C(5)–C(4)	111.8(9)
S(2)–Tl(2)–C(14)	93.6(3)	S(2)–C(8)–N(3)	125.7(6)
N(1)–Tl(2)–C(13)	96.7(3)	S(2)–C(8)–C(9)	120.1(7)
N(1)–Tl(2)–C(14)	85.8(3)	N(3)–C(8)–C(9)	114.1(7)
C(13)–Tl(2)–C(14)	164.9(4)	O(2)–C(9)–C(8)	120.5(8)
C(2)–O(1)–C(5)	106.4(7)	O(2)–C(9)–C(10)	108.1(9)
C(9)–O(2)–C(12)	108.2(8)	C(8)–C(9)–C(10)	131.4(8)
N(2)–N(1)–C(1)	117.9(7)	C(9)–C(10)–C(11)	107.4(8)
N(4)–N(3)–C(8)	118.5(8)	C(10)–C(11)–C(12)	108(2)
S(1)–C(1)–N(1)	123.0(6)	O(2)–C(12)–C(11)	107.9(9)
S(1″)–Tl(1)–N(4′)	149.3(2)	O(1)–Tl(2)–O(2)	82.0(2)
S(1)–Tl(1)–S(1″)	75.09(7)		

Results and discussion

Description of the structure

The two thallium atoms of each asymmetric unit (Tl(1) and Tl(2), see Fig. 1) have dissimilar coordination spheres. Tl(1) is bound to the methyl groups with which it forms a normal $TlMe_2$ unit and to the S(1) and N(2) atoms of a chelate ligand (L(1)). The distance Tl(1)–N(2)H_2 is between those observed for thallium amino bonds in $TlMe_2$(L-PHE) and $TlMe_2$(DL-TRP)·H_2O (PHE = phenylalanine, TRP = tryptophanato) [11]. The Tl(1)–S(1) bond is longer than in $TlMe_2$(L)·HL (where HL = cyclopentanone thiosemicarbazone) [2].

Tl(2) is bound to N(1) of the molecule that is chelated to Tl(1) (L(1)) and to S(2′) of L(2′), a ligand molecule belonging to another asymmetric unit and related with L(2) by the symmetry operation $(0.5+x)-1$, $0.5-y$, $(0.5-z)-1$. The distance Tl(2)–S(2′) is slightly shorter than Tl(1)–S(1) while Tl(2)–N(1) is longer than Tl(1)–N(2). Like Tl(1)Me_2 the Tl(2)Me_2 unit has normal structural parameters. Interatomic distances shorter than the corresponding sums of van der Waals radii [12] (Table 2) show that both thallium atoms also have additional weak interactions. Tl(1) interacts with N(4′) of L(2′), and with S(1″) of L(1″), a molecule related to L(1) by the symmetry operation $-x$, $-y$, $(-z+1)$); while Tl(2) interacts with O(1) of L(1) and with N(3) and O(2) of L(2). If these secondary bonding interactions are considered, Tl(1) has a rather distorted octahedral environment and Tl(2) a distorted bipyramidal pentagonal coordination sphere (see Fig. 1).

Like Tl(1) and Tl(2), L(1) and L(2) also differ. L(1) is very planar ($\chi^2=35$) whereas for L(2), $\chi^2=1986$, the S(2)C(8)N(3)N(4)C(9) plane ($\chi^2=6$) making an angle of 21(2)° with the plane of the ring C(9)C(10)C(11)C(12)O(2). Moreover, although differences in bond lengths are of the same order as the e.s.d.s, there are significant dissimilarities in bond angles. The angle S(1)C(1)N(1) is narrower than S(2)C(8)N(3), no doubt due to L(1) chelating Tl(1); the narrowing of this angle widens C(2)C(1)N(1), but leaves C(2)C(1)S(1) practically the same as C(9)C(8)S(2). Similarly, the weak interaction through O(1), which gives L(1)–Tl(2) bonding an asymmetrically bidentate character, makes O(1)C(2)C(1) narrower than O(2)C(9)C(8).

Structurally the compound can be described as formed of approximately planar strips in which alternate L(2) and Tl(2)Me_2 units are linked through N(3) and S(2), with L(1) and Tl(1) periodically incorporated collaterally; adjacent strips lie on different, parallel planes and are linked by weak sulfur bridges. The packing in the lattice is shown in Fig. 2.

IR spectra

Table 4 shows the assignments [13–15] of the main IR bands of the ligand and the complexes prepared.

The main features of the IR spectrum of the free ligand are identical to those described by Keshari and Mishra [13]. The positions of the bands differ to a greater or lesser extent from those reported by other authors (for example, $\delta(NH_2)$ is at 1590 cm^{-1} (no bands in the range 1600–1700 cm^{-1}) whereas Singh *et al.* [14] found this band at 1630 cm^{-1}); the discrepancies are probably due to the presence of different conformers in the solid samples examined.

The IR data for $TlMe_2fth$ agree with the coordination scheme shown by the X-ray study (*vide supra*). The intensity of $\nu(NH_2)$ increase, as is expected when the NH_2 group coordinates to a metal [16]; the shift in $\nu(NH_2)$ to a higher wavenumber than in the free ligand

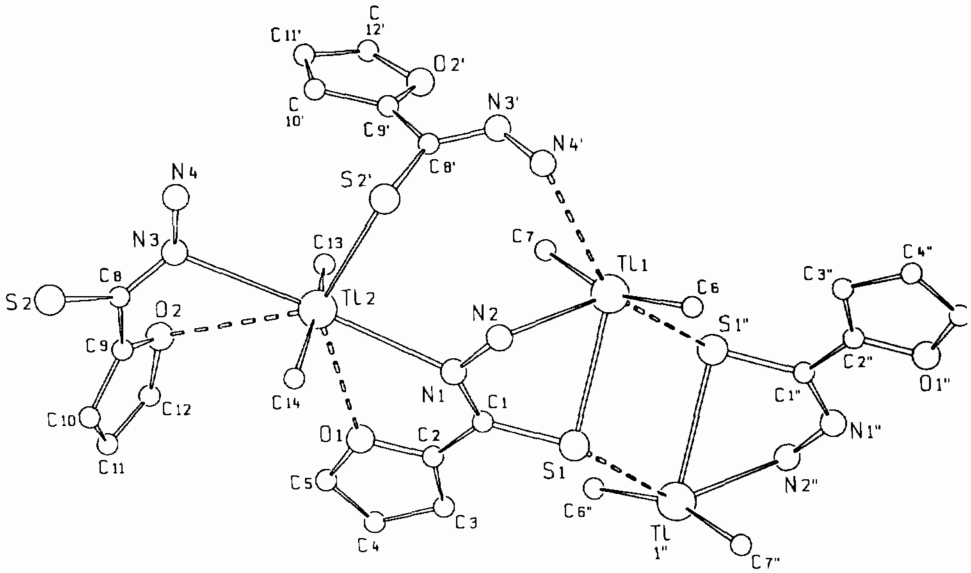

Fig. 1. SCHAKAL plot of $TlMe_2$fth, showing the coordination of Tl(1) and Tl(2) and the numbering scheme. Bond distances longer than 2.95 Å are represented as dashed lines.

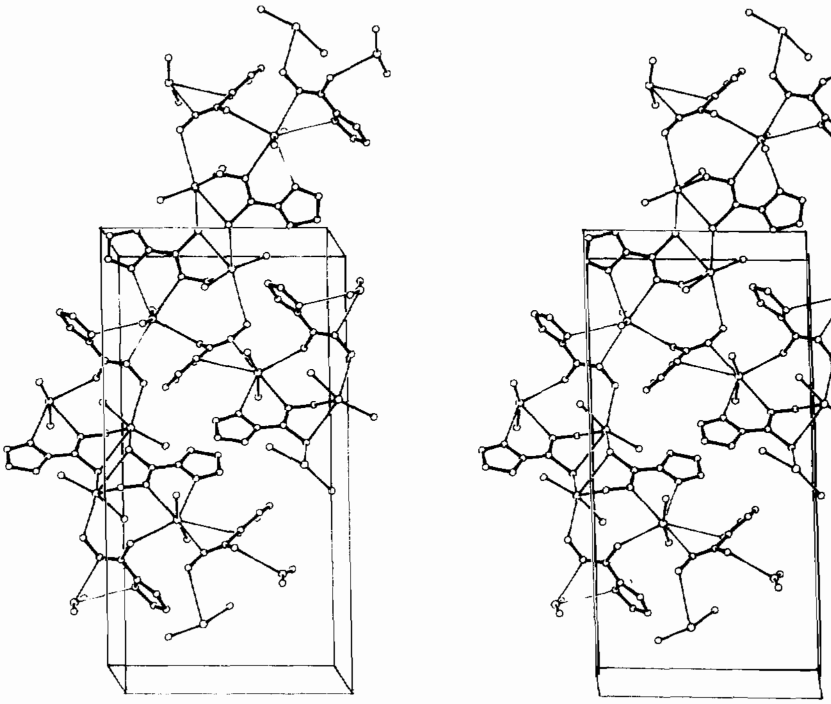

Fig. 2. ORTEP stereoscopic view of the packing in the lattice of $TlMe_2$fth.

may be due to the amino group being involved in hydrogen bonding in the free ligand but not in the thallium compound.

Coordination via S produces a slight shift in ν(C=S) to lower wavenumbers. Although bands in the range 1300–1000 cm^{-1} undergo slight shifts and variations in intensity upon coordination, we were unable to identify 'thioamide band III'. The coordination of the furan O atom to the metal is too weak to change the position or the intensity of the ring bands, even ν(C–O) [14].

In HgMefth, the shifts in ν(C=S) and ν(C–N) are similar to those observed in $TlMe_2$fth suggesting coordination of Hg to S and, probably, N(1). The position and intensity of $\nu(NH_2)$ suggest there is no coordination via the NH_2 group. Nor is there evidence of coordination of the furan ring.

TABLE 4. Most significant bands (cm^{-1}) in the IR spectra of the ligand and complexes

Hfth	HgMefth	$TlMe_2fth$	Assignment
3240m	3140m	3320m-s	$\nu(N{-}H) + \nu(NH_2)$
3180m		3250m-s	
3140m		3140m	
1590s	1610s	1605m	$\delta(NH_2)$
		1580m	
1560m	1570m	1570m	$\delta(NH) + \nu(C{-}N)$
1320s	1360m	1380m	$\nu(C{-}N) + \delta(N{-}H)$
		1310m	
760s	750s	750m	$\nu(C{=}S)$
		730m	
	775m,b	790s,b	$\rho(CH_3)$
		530m	$\nu_{as}(C{-}Tl{-}C)$
		470w	$\nu_{sym}(C{-}Tl{-}C)$
	530m		$\nu(Hg{-}C)$

s = strong; m = medium; b = broad; w = weak.

With regard to the organometallic fragments of the two complexes, $\rho(CH_3)$, $\nu_{as}(C{-}Tl{-}C)$, $\nu_s(C{-}Tl{-}C)$ and $\nu(Hg{-}C)$ are all located near the positions reported for other complexes with related ligands [1].

Conductivity

The compounds are insoluble in water but soluble in DMSO. The mercury derivative is also soluble in $CDCl_3$. The conductivity of HgMefth in DMSO (see 'Experimental') suggests that it is non-ionogenous. The value obtained for the thallium complex suggests significant ionicity, even though it is below the lower limit of the reported range for 1:1 electrolytes [17].

NMR spectra

^1H, ^{13}C, ^{199}Hg and ^{205}Tl NMR data are shown in Table 5. No N(1)H signal is present in the spectra of the complexes, showing that the ligand is deprotonated.

Coordination shields the ring protons and deshields the $-NH_2$ group, probably because of a thione-to-thiol change; both effects are greater in the mercury compound. For HgMefth, $^2J(^1H{-}^{199}Hg)$ is in the typical range for a methylmercury cation bound to a deprotonated –SH group [18]. $^2J(^1H{-}^{205}Tl)$ is clearly different from the coupling constant for $TlMe_2ClO_4$ in the same solvent [19], supporting the conductimetric evidence that in DMSO the dimethylthallium(III) cation remains at least partially coordinated to the ligand.

The most interesting feature of the ^{13}C NMR spectra is the change in the C(1) signal, which is shielded when the organometallic compounds are formed. This is a good indication of the thione-to-thiol change mentioned above [20], which seems to be greater in the mercury derivative (Table 5). In methylmercury(II) compounds the coupling constant $^1J(^{13}C{-}^{199}Hg)$ is very sensitive to the identity of the atom *trans* to the methyl group, to the solvent and, according to theoretical arguments, to the coordination number of the metal (since it can modify the participation of the mercury 6s orbital in the hybrid orbital involved in the C–Hg bond [20]). The value observed for HgMefth in DMSO-d_6 (Table 5) is lower by *c.* 100 Hz than in the neutral S-bound complexes of Hg with 6-mercaptopurine riboside or 2-mercaptobenzoxazole [21, 22]. The greater value observed in $CDCl_3$ is greater than in S-bound 2-mercaptopyridine derivatives [23]. These differences may be due, at least in part, to Hg binding to other atoms as well as S in non-coordinating solvents (e.g. there may be fast interchange between S- and N(1)-bonded species). The linebroadening of the ^{199}Hg signal in deuterochloroform (Table 5) supports this idea [24].

$^1J(^{13}C{-}^{205}Tl)$ is very similar to the value observed in the thiophenol derivative, although the thallium nuclide is more shielded than in the latter compound [6]. Both $^1J(^{13}C{-}^{205}Tl)$ and $\delta(Tl)$, the latter especially, differ from the values reported for $TlMe_2ClO_4$ [19]. In general, in

TABLE 5. Multinuclear NMR parameters for the ligand and complexes[a]

Complex	Solvent	N(1) H	$N(2)H_2$	C(3)H	C(4)H	C(5)H	MRn	$^2J(^1H{-}M)$	
Hfth	DMSO-d_6	12.07 sb[b](1)[c]	6.13 sb(2)	7.03 d(1)	6.58 dd(1)	7.81 d(1)			
HgMefth	DMSO-d_6		6.64 s(2)	6.67 d(1)	6.47 dd(1)	7.62 d(1)	0.61 s(3)	180.6	
$TlMe_2fth$	DMSO-d_6		6.21 s(2)	6.56 dd(1)	6.34 dd(1)	7.49 t(1)	0.76 d(6)	414.1	
		C(1)	C(2)	C(3)	C(4)	C(5)	MRn	$^1J(^{13}C{-}M)$	M
Hfth	DMSO-d_6	168.99	150.73	112.33	114.38	114.52			
HgMefth	DMSO-d_6	154.14	136.35	111.28	108.25	142.50	10.38	1374.8	−576.5[d](63)[e]
	$CDCl_3$	153.41	134.51	111.32	110.14	142.87	11.91	1496.3	−542.0[f](92)
$TlMe_2fth$	DMSO-d_6	156.43	146.77	107.69	110.79	141.19	21.58	2893.2	3775.5[g](2426)

[a] δ in ppm referred to the solvent signal for ^1H and ^{13}C NMR spectra, to 95% $HgMe_2$ in Et_2O for ^{199}Hg NMR; and to an aqueous solution of $TlClO_4$ extrapolated to infinite dilution for ^{205}Tl NMR. *J* values in Hz. Numbering scheme: see 'Introduction'. [b] b = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet. [c] Number of protons from integrated intensities. [d] 0.16 M solution. *S*/*N* = 52. [e] $w_{1/2}$. [f] 0.20 M solution. *S*/*N* = 52. [g] 0.14 M solution.

DMSO the carbon–thallium coupling constant seems not to be very sensitive to the identity of the ligand in dimethylthallium(III) compounds: simple salts [19] and thiolates [6] have values in an apparently non discriminating sequence in the range 2890–3010 Hz, although some complex salts are exceptions (see for example ref. 20). This relative insensitivity is possibly due to the ionogenic and coordinating nature of the solvent, and to the fact that the hybridization scheme of the $TlMe_2$ group generally changes rather little when the ligand changes as is reflected by the usually almost linear C–Tl–C angle. On the other hand, the ^{205}Tl nuclide is deshielded on going from simple salts [19] to thiolates [6] or thiosemicarbazonates [25], with shifts as large as 300–400 ppm in comparison with dimethylthallium(III) perchlorate. Nevertheless, the influence of the ligand characteristics (basicity, donor atom identity, coordination number, etc.) remain to be explored.

Supplementary material

Anisotropic thermal parameters, observed and calculated structure factors and a full list of bond distances and angles are available from the authors upon request.

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