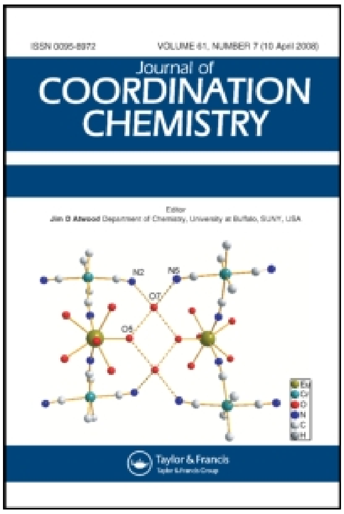

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MONO-ORGANOMERCURY AND DIORGANOTHALLIUM DERIVATIVES OF THIOHYDANTOIN AND 5-(BENZYLIDENE)-2-THIOHYDANTOIN: THE CRYSTAL STRUCTURE OF DIMETHYL-[5-(BENZYLIDENE)-2-THIOHYDANTOINATO]-THALLIUM(III)

José S. Casas[a]; Eduardo E. Castellano[b]; M. Delfina Couce[c]; Nuria Playá[a]; Agustín Sánchez[a]; José Sordo[a]; José M. Varela[a]; Julio Zukerman-Schpector[b]
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(Received 31 March 1998)

The complexes [$TlR_2(Td)$], [$TlR_2(BTd)$], [HgR(Td)] and [HgR(BTd)] (R = Me, Ph; HTd = thiohydantoin; HBTd = 5-(benzylidene)-2-thiohydantoin) were prepared by reacting the appropriate ligand with the appropriate diorganothallium hydroxide or mono-organomercury acetate. They have been studied in the solid state (by vibrational spectroscopy and mass spectrometry) and in solution (by using NMR). In addition, the crystal structure of [$TlMe_2(BTd)$] has been determined by X-ray diffraction. The crystals have a polymeric structure in which each thallium atom is coordinated to the two methyl C atoms, the S and N atoms of one BTd ligand, the S atom of another and the O atom of a third. The coordination modes of the two ligands in the other complexes are discussed on this basis in the light of spectroscopic data.

Keywords: Mono-organomercury(II); diorganothallium(III); thiohydantoin; complexes; crystal structure; NMR

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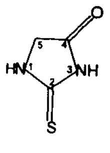
INTRODUCTION

Among complexes of the cation $TlMe_2^+$ with ligands subject to the tautomeric equilibrium $-NH-C(S)- \rightleftarrows -N{=}C(SH)-$, Tl exhibits an interesting variety of coordination numbers and environments, especially among ligands that also contain other donor atoms.[1] Notably, crystals of $[TlMe_2(PyTd)]$, the $TlMe_2^+$ complex of the 5-(2-pyridinylmethylene) derivative (HPyTd) of 2-thiohydantoin (imidazolidin-4-one-2-thione, HTd) exhibit desmotropism; the PyTd ligand exist in two desmotropic forms: one results from deprotonation of HPyTd at N(3) and the other results from deprotonation of HPyTd at N(1). This fact leads to two different coordination modes and two types of Tl environment.[1g] To test whether it is essentially the influence of the pyridinyl nitrogen that is responsible for the coordination of HPyTd *via* its thiohydantoin N(1) as well as *via* N(3) (the expected donor, N(3)–H being the more acidic N–H group[2]), or whether a significant role may also be played by other factors such as the bulkiness of the pyridinyl moiety, we have now prepared complexes of this cation with thiohydantoin (HTd, **I**) and 5-(benzylidene)-2-thiohydantoin (HBTd, **II**) and determined the crystal structure of the 5-(benzylidene)-2-thiohydantoin derivative. To allow comparison with the effect of a bulky organocation, we also prepared both dimethyl and diphenylthallium complexes of HTd. In addition, since work on rhodanine complexes[1d] has shown interesting spectroscopic differences between dimethylthallium(III) and methylmercury(II) complexes in solution we likewise prepared complexes of methyl- and phenylmercury(II) with both ligands. This paper describes the preparation and characterization of these complexes and the crystal structure of dimethyl-[5-(benzylidene)-2-thiohydantoinato]thallium(III).



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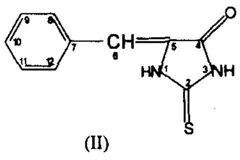

(II)

EXPERIMENTAL

HBTd was obtained by aldol condensation of 2-thiohydantoin with benzaldehyde.[3] Dimethylthallium and diphenylthallium hydroxides were obtained from the respective iodide and bromide[4] by reaction with an aqueous suspension of freshly precipitated Ag_2O. All other chemicals and organic solvents used for synthesis work were commercial products of reagent grade.

[TlMe$_2$(Td)]

An aqueous solution of dimethylthallium hydroxide (0.70 g, 2.76 mmol) was added dropwise to a solution of HTd (0.32 g, 2.77 mmol) in methanol. The mixture was stirred for 24 h and the violet product was isolated by filtration and dried *in vacuo*. M.p. 180°C (dec.). Found: C, 17.2; H, 2.6; N, 8.0; Tl 58.5%. $C_5H_9N_2OSTl$ requires C, 18.0; H, 2.5; N, 7.5; Tl, 57.8%. Mass spectrum: 335 ($C_4H_6N_2OSTl$, 72.9); 320 ($C_3H_3N_2OSTl$, 6.5); 235 (C_2H_6Tl, 20.2); 220 (CH_3Tl, 15.2); 205 (Tl, 100). IR spectrum (cm^{-1}): 3244m, 3136m, ν(N–H); 1638vs, ν(C=O); 1447mb, 1325m, 1290m, ν(C–N–C); 1175s, $\delta_{sym}(CH_3)$; 1138m, 784m, ν(C=S); 807m, $\rho(CH_3)$; 547m, ν_{asym} (C–Tl–C); 413m, ν(Tl–O); 334m, ν(Tl–S). Λ_M 13.1 $S\,cm^2\,mol^{-1}$.

[TlPh$_2$(Td)]

A fresh aqueous solution of diphenylthallium hydroxide (0.86 g, 2.28 mmol) was reacted with a methanolic solution of HTd (0.26 g, 2.28 mmol). After the reaction was completed, the mixture was stirred for 48 h before being filtered. M.p. 195°C (dec.). Found: C, 38.1; N, 6.3; H, 3.0; Tl 43.4%. $C_9H_{13}N_2OSTl$ requires C, 38.0; N, 5.9; H, 2.7; Tl, 43.2%. IR spectrum (cm^{-1}): 3138 m, ν(N–H); 1669s, ν(C=O); 1529m, 1296s, ν(C–N–C); 1156sh, 785sh, ν(C=S); 395m,b, ν(Tl–O); 325s, ν(Tl–S). Λ_M 5.6 $S\,cm^2\,mol^{-1}$.

[HgMe(Td)]

Solid methylmercury acetate (1.00 g, 3.64 mmol) was added to a solution of HTd (0.42 g, 3.64 mmol) in methanol and the mixture was stirred at room temperature for 24 h. The beige powdery product was collected by filtration, washed with methanol and dried *in vacuo* over calcium chloride. M.p. 176°C. Found: C, 14.9; H, 1.9; N, 8.3%. $C_4H_6N_2OSHg$ requires C, 14.5; H, 1.8; N, 8.5%. Mass spectrum: 464 ($C_2H_6SHg_2$, 7.0); 449 (CH_3SHg_2, 4.1); 402 (Hg_2, 2.0); 332 ($C_4H_6N_2OSHg$, 33.9); 234 (SHg, 4.8); 217 (CH_3Hg, 32.6); 202 (Hg, 31.6); 116 ($C_3H_4N_2OS$, 100). IR spectrum (cm^{-1}) 3222 sb, ν(N–H); 1672vs, ν(C=O) ; 1520m, 1318m, ν(C–N–C); 1170s, $\delta_{sym}(CH_3)$; 1120w, 742sh, ν(C=S); 794m, $\rho(CH_3)$; 555m, ν(Hg–C); 331m, ν(Hg–S). Λ_M 0.3 $S\,cm^2\,mol^{-1}$.

[HgPh(Td)]

This was carried out, as for [HgMe(Td)] but using 0.34 g (2.97 mmol) of HTd and 1.00 g (2.97 mmol) of phenylmercury acetate. M.p. 194°C (dec.). Found: C, 27.5; H, 2.0; N, 7.1%. $C_9H_8N_2OSHg$ requires C, 27.5; H, 2.2; N, 6.9%. Mass spectrum: 356 ($C_{12}H_{10}Hg$, 1.0); 279 (C_6H_5Hg, 2.5); 202 (Hg, 9.0); 78 (C_6H_6, 100). IR spectrum (cm^{-1}): 3195s,b, ν(N–H); 1685vs, ν(C=O); 1479, 1299, ν(C–N–C); 1120w, 740m, ν(C=S); 336sh, ν(Hg–S); 255m, ν(Hg–C). Λ_M 0.2 S $cm^2 mol^{-1}$.

[$TlMe_2$(BTd)]

An aqueous solution of $TlMe_2OH$ (0.35 g, 3.98 mmol) was added slowly, with stirring, to an equimolar amount of HBTd (0.28 g) dissolved in acetone-ethanol. After 48 h of stirring, the solution was left to concentrate slowly in air, to afford red crystals that were studied by X-ray diffraction. M.p. 204°C. Found: C, 33.5; H, 3.3; N, 6.4; Tl, 47.0%. $C_{12}H_{13}N_2OSTl$ requires: C, 32,9; H, 3.0; N, 6.4; Tl, 46.7%. Mass spectrum: 438 ($C_{12}H_{13}N_2OSTl$, 3.6); 423 ($C_{11}H_{10}N_2OSTl$, 5.6); 408 ($C_{10}H_7N_2OSTl$, 8.9); 235 (C_2H_6Tl, 29.6); 205 (Tl, BTd, 49.9); 117 ($C_3H_5N_2OS$, 100). IR spectrum (cm^{-1}): 3185m, ν(N–H); 1682s, ν(C=O); 1282m, ν(C–N–C); 1175s, $\delta_{sym}(CH_3)$; 1157m, 832w, ν(C=S); 804m, $\rho(CH_3)$; 544m, ν_{asym}(C–Tl–C); 402w, ν(Tl–O); 339m, ν(Tl–S). Λ_M 18.8 S $cm^2 mol^{-1}$.

[HgMe(BTd)]

Methylmercury acetate (0.37 g, 1.82 mmol) was added to a solution of HBTd (0.5 g, 1.82 mmol) in acetone–ethanol and the mixture was stirred for 24 h. The beige solid that formed was separated by filtration, washed with ethanol and dried *in vacuo* over calcium chloride. M.p. 227–230°C. Found: C, 31.1; H, 2.3; N, 6.5%. $C_{11}H_{10}N_2OSHg$ requires: C, 31,5; H, 2.4; N, 6.7%. Mass spectrum: 464 (C_2H_6SHg, 6.4); 449 (CH_3SHg, 3.9); 434 (SHg_2, 1.3); 402 (Hg_2, 2.0); 249 (CH_3SHg, 4.0); 232 (C_2H_6Hg, 15.1); 217 (CH_3Hg, 35.8); 204 ($C_8H_{10}NOS$, 100); 202 (Hg, 5.2). IR spectrum (cm^{-1}): 3177m, ν(N–H); 1699s, ν(C=O); 1259m, ν(C–N–C); 1171, $\delta_{sym}(CH_3)$; 832w, ν(C=S); 771m, $\rho(CH_3)$; 363 m, ν(Hg–S). Λ_M 0.3 S $cm^2 mol^{-1}$.

[HgPh(BTd)]

HgPhAc (0.83 g, 2.45 mmol) was added to a solution of HBTd (0.50 g, 2.45 mmol) in ethanol and the mixture was stirred for 48 h. The beige solid that formed was treated like the methylmercury derivative. M.p. 240°C. Found: C, 40.0; H, 2.5; N, 5.7%. $C_{16}H_{12}N_2OSHg$ requires: C, 40,0; H, 2.5; N, 5.8%. Mass spectrum: 356 ($C_{12}H_{10}Hg$, 15.4); 279 (C_6H_5Hg, 7.9); 202 (Hg, 3.7); 77 (C_6H_5, 100). IR spectrum (cm^{-1}): 3180m, ν(N–H) ; 1710s, ν(C=O); 1264m, ν(C–N–C); 832w, ν(C=S); 375m, ν(Hg–S); 255w, ν(Hg–C). Λ_M 0.3 S $cm^2 mol^{-1}$.

Physical Measurements

Carbon, hydrogen and nitrogen were determined in a Carlo-Erba EA-1108 apparatus, and thallium was determined with a Varian A30 atomic absorption spectrometer after digestion with hydrogen peroxide/sulphuric acid. Melting points were measured with a Büchi apparatus and are uncorrected. IR spectra (in KBr Pellets or Nujol mulls) were recorded on a Bruker IFS66V FT-IR spectrometer. Mass spectra were obtained under EI conditions (direct insertion probe, 70 eV, 250°C) on a Kratos MS50TS spectrometer connected to a DS-90 data system; fragments were identified using DS 90 software (for each compound we indicate at least the base peak and the main metallated ion, if detected, together with the percentage relative abundance). ^1H, ^{13}C and ^{199}Hg NMR spectra were recorded (the latter at 44.8 MHz in 10 mm tubes) on a Bruker WM-250 spectrometer and ^{205}Tl spectra at 230.8 MHz (in 10 mm tubes) on a Bruker AM-400 apparatus. Conductivities (DMSO, 10^{-3} M) were measured with a WTW LF-3 conductivity meter.

Determination of the Crystal Structure of [$TlMe_2$(BTd)]

A suitable crystal of irregular shape with maximum and minimum dimensions 0.50 and 0.10 mm was obtained as described above. *Crystal data*: $C_{12}H_{13}N_4OSTl$, $M = 437.68$, monoclinic, $a = 8.941(4)$, $b = 12.534(2)$, $c = 12.279(6)$ Å, $\beta = 100.83(3)°$, $U = 1352(1)$ Å^3, $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, space group $P2_1/n$ (No 14), $Z = 4$, $D_{\text{calcd}} = 2.151$ g cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 122.07$ cm^{-1}; $F(000) = 816$, $T = 293$ K.

Data Collection and Processing

A CAD 4 diffractometer was used; $\omega/2\theta$ mode with variable scan width and scan speed graphite-monochromated Mo-K_α radiation; 3706 reflections measured ($0 > \theta > 30°$); 3575 unique [$R = 0.024$ after empirical absorption correction (max. and min. transmission factors 1.71, 0.71)], giving 2603 with $I > 3\sigma(I)$.

TABLE I Fractional atomic coordinates and equivalent isotropic temperature factors (Å^2) for the structure

Atom	*X/A*	*Y/B*	*Z/C*	B_{iso}
Tl	0.2444(1)	0.1524(1)	0.2084(1)	2.687(9)
S	0.2361(3)	0.3810(2)	0.2535(2)	3.86(7)
O	−0.0843(9)	0.3744(4)	0.5443(6)	4.8(2)
N(1)	0.0656(7)	0.2373(4)	0.3374(5)	2.4(2)
N(3)	0.0678(9)	0.3995(5)	0.4150(6)	3.3(2)
C(2)	0.119(1)	0.3343(5)	0.3354(7)	2.8(2)
C(4)	−0.024(1)	0.3419(5)	0.4697(7)	3.1(2)
C(5)	−0.0282(9)	0.2334(5)	0.4176(6)	2.3(2)
C(6)	−0.1166(9)	0.1564(5)	0.4470(7)	2.5(2)
C(7)	−0.1497(8)	0.0498(6)	0.3988(7)	2.5(2)
C(8)	−0.101(1)	0.156(7)	0.3041(8)	4.0(3)
C(9)	−0.139(1)	−0.0878(7)	0.2627(9)	4.8(4)
C(10)	−0.224(1)	−0.1542(7)	0.3151(9)	4.1(3)
C(11)	−0.275(1)	−0.1183(7)	0.4083(9)	4.4(3)
C(12)	−0.238(1)	−0.172(6)	0.4517(7)	3.2(3)
C(Me$_1$)	0.450(1)	0.1396(8)	0.325(1)	4.7(3)
C(Me$_2$)	0.058(1)	0.1400(8)	0.0732(8)	4.7(3)

Structure Analysis and Refinement

The structure was solved using the heavy atom Patterson method and difference Fourier techniques. In the final cycles of full-matrix least-squares refinement all non-H atoms were treated anisotropically. Data were corrected for Lp and absorption.[5] $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.040$ and $R_W = [\sum w\,(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.039$, $w = \sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$. A final difference Fourier map showed peaks of maximum density 1.81 e Å^{-3} around the Tl atom. Scattering factors for non-H atoms were taken from Cromer and Mann[6] and corrections for anomalous dispersion from Cromer and Liberman.[7] Data processing was performed using the SHELX 76[8] and ZORTEP software packages.[9] Final atomic coordinates are listed in Table I.

RESULTS AND DISCUSSION

Description of the Structure of [TlMe$_2$(BTd)]

A view of the molecule indicating the atom numbering scheme is shown in Figure 1. The thallium atom is coordinated to the two methyl C atoms, to the S and N(1) atoms of one BTd ligand, to the S atom (S^i) of a second, and to the O atom (O^{ii}) of a third (for the symmetry operations i and ii, see Table II, which lists the relevant bond distances and angles around the thallium atom). The Tl interactions constitute a three dimensional network

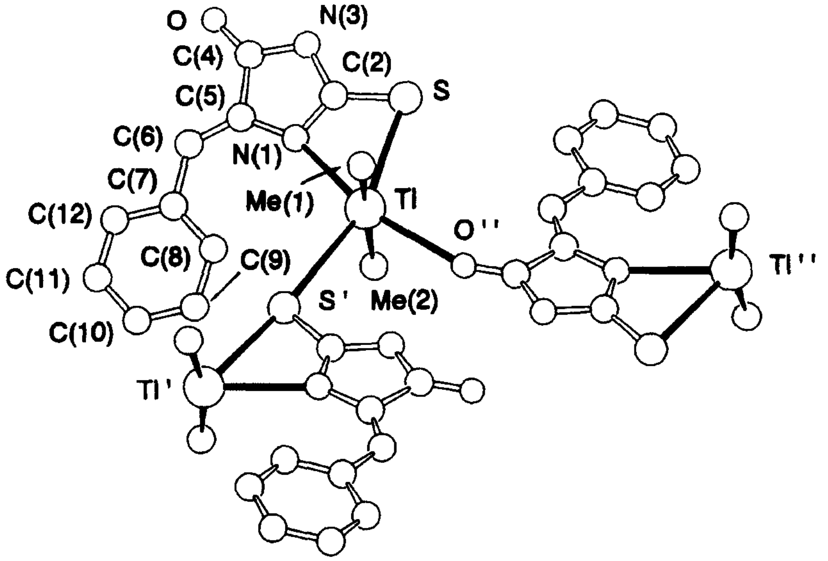

FIGURE 1 The crystal structure of [$TlMe_2(BTd)$].

creating a $TlMe_2(BTd)$ (see Figure 2) polymer with a structure closely resembling that of [$TlMe_2(DABRd)$].[1e]

The thallium interactions define a very distorted octahedron similar to that previously found in [$TlMe_2(DABRd)$].[1e] The Tl–C and Tl–N distances are similar in these two TlC_2NS_2O cores, but the Tl–S bond is shorter and the Tl–O^{ii} and Tl–S^{i} bonds longer in [$TlMe_2(BTd)$] than in [$TlMe_2$-$(DABRd)$]; in particular, Tl–S^{i} is very long [3.434(2) Å], although it is still shorter than the sum of the Van der Waals radii (3.76 Å)[10] and slightly shorter than in some other systems.[1f] The deviation of the C–Tl–C angle from linearity, 12°, is less than the 13.8° found in the DABRd derivative. The TlSN(1) $S^{i}O^{ii}$ structure is roughly planar ($\chi^2 = 24.1$) with the Tl atom 0.059(1) Å from the least squares plane, the maximum deviation from which is that of the S atom (– 0.282 Å); the greatest distorsion in this structure is the narrowing of the S–Tl–N(1) angle to 57.2(1)° due to the bite of the BTd ligand.

Although the more acidic of the two N–H groups of HTd is N(3)–H,[2] in [$TlMe_2(BTd)$] the BTd ligand coordinates through the N(1) atom. It seems possible that the presence of the N(3)-protonated complex in solution may be favoured by the unsaturated C(5) side chain,[11] and that the exclusive crystallization of this form, rather than the N(1)-protonated form that is

TABLE II Selected bond lengths (Å) and angles (°) in [TlMe$_2$(BTd)]

Bond distances			
Tl–S	2.922(2)	N(3)–C(4)	1.36(1)
Tl–N(1)	2.674(6)	C(4)–C(5)	1.50(1)
Tl–C(Me$_1$)	2.11(1)	C(5)–C(6)	1.34(1)
Tl–C(Me$_2$)	2.13(1)	C(6)–C(7)	1.47(1)
Tl–O^{ii}	2.771(7)	C(7)–C(8)	1.38(1)
Tl–S^{i}	3.434(2)	C(7)–C(12)	1.39(1)
S–C(2)	1.687(9)	C(8)–C(9)	1.41(1)
O–C(4)	1.22(1)	C(9)–C(10)	1.37(1)
N(1)–C(2)	1.308(9)	C(10)–C(11)	1.38(1)
N(1)–C(5)	1.41(1)	C(11)–C(12)	1.39(1)
N(3)–C(2)	1.41(1)		
Bond angles			
S–Tl–N(1)	57.2(1)	S–C(2)–N(3)	121.9(6)
S–Tl–C(Me$_1$)	89.8(3)	N(1)–C(2)–N(3)	110.9(7)
S–Tl–C(Me$_2$)	100.1(3)	O–C(4)–N(3)	126.0(8)
S–Tl–O^{ii}	107.1(1)	O–C(4)–C(5)	130.2(8)
S–Tl–S^{i}	161.46(6)	N(3)–C(4)–C(5)	103.9(7)
N(1)–Tl–C(Me$_1$)	99.8(3)	N(1)–C(5)–C(4)	107.2(6)
N(1)–Tl–C(Me$_2$)	91.3(3)	N(1)–C(5)–C(6)	132.2(7)
N(1)–Tl–O^{ii}	162.3(2)	C(4)–C(5)–C(6)	120.5(7)
N(1)–Tl–S^{i}	109.5(1)	C(5)–C(6)–C(7)	129.1(7)
C(Me$_1$)–Tl–C(Me$_2$)	168.0(4)	C(6)–C(7)–C(8)	123.3(7)
C(Me$_1$)–Tl–O^{ii}	87.4(3)	C(6)–C(7)–C(12)	116.7(7)
C(Me$_1$)–Tl–S^{i}	79.5(3)	C(8)–C(7)–C(12)	120.0(8)
C(Me$_2$)–Tl–O^{ii}	83.3(3)	C(7)–C(8)–C(9)	119.7(9)
C(Me$_2$)–Tl–S^{i}	92.7(3)	C(8)–C(9)–C(10)	121(1)
O^{ii}–Tl–S^{i}	87.6(1)	C(9)–C(10)–C(11)	119.3(9)
C(2)–N(1)–C(5)	108.2(6)	C(10)–C(11)–C(12)	121.4(9)
C(2)–N(3)–C(4)	109.8(7)	C(7)–C(12)–C(11)	119.0(8)
S–C(2)–N(1)	127.1(6)		

Symmetry operations: (i) $\frac{1}{2}-x$; $-\frac{1}{2}+y$; $\frac{1}{2}-z$ (ii) $\frac{1}{2}+x$; $\frac{1}{2}-y$; $-\frac{1}{2}+z$.

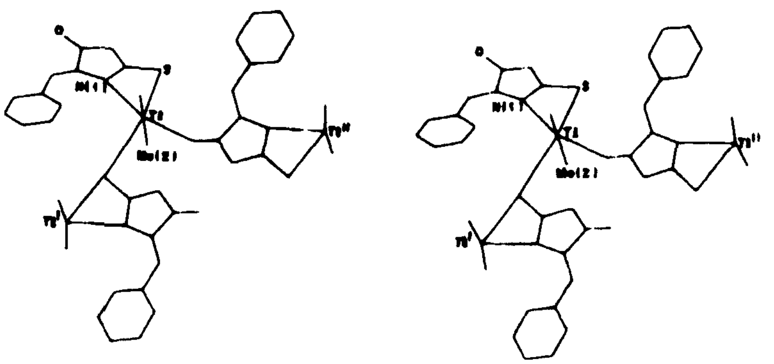

FIGURE 2 A stereoscopic view of [TlMe$_2$(BTd)].

presumably also present in solution, may be due simply to lower solubility. In the case of [$TlMe_2$(PyTd)] too, both forms would be present in solution, but the fact that both forms are also present in the crystals suggests that the N(3)-protonated form is no less soluble than the other; rather, it may be the influence of the pyridinyl nitrogen that prevents exclusive crystallization of a more soluble N(1)-protonated form, so that the observed crystallographic desmotropism is the manifestation of the balance between these two factors.

The BTd ligand is not planar, the practically planar 2-thiohydantoin ring ($\chi^2 = 11.3$) making a diedral angle of 9.2° with the planar phenyl group. In the 2-thiohydantoin moiety the C(2)–S bond is longer than in the thione-free HTd[12] but shorter than in thiolic 2-S-methyl-5, 5-dimethylimidazolin-4-one (MeS–Me_2Td),[13] suggesting incomplete evolution to the thiol form; in fact, the C(2)–N(3) and C(2)–N(1) distances do not differ significantly from those found in HTd, and the N(1)–C(2)–N(3) angle [110.9(9)°] is slightly closer to the 106.8° of HTd than to the 115.5° of MeS–Me_2Td.

IR Spectra

The IR bands that are most relevant for inferring the protonation states and coordination of the complexes other than [$TlMe_2$(BTd)] [HTd: 3282s, ν(N–H); 3190s, ν(N–H); 1720vs, ν(C=O); 1530s, ν(C–N–C) + δ(N–H); 1299, ν(C–N–C); 1157s, 891m, ν(C=S); HBTd: 3233sb, ν(N–H); 1724vs, ν(C=O); 1254m, ν(C–N–C); 1155m, 832m, ν(C=S)] were assigned following Cogrossi's interpretation of the spectrum of thiohydantoin.[14] Note that in the HBTd spectrum only a single broad N–H stretching band was identifiable and the ν(C–N–C) + δ(N–H) band was indistinguishable among 5-benzylidene bands.

The crystallographically determined coordination of the thallium atom to the O, S and N(1) atoms in [$TlMe_2$(BTd)] shifts ν(C=O) to lower wavenumbers and ν(C–N–C) to higher wavenumbers, and dampens the ν(C=S) bands. In [$TlPh_2$(Td)], O-coordination is suggested by the shift of ν(C=O) to lower wavenumbers than in HTd, and S-coordination by the weakening of the ν(C=S) bands and the shift of the less energetic of the two to lower wavenumbers; N-coordination is called into doubt by the fact that the ν(C–N–C) bands remain almost unshifted [the loss of intensity by the band at 1530 cm^{-1} is attributable to loss of its δ(N–H) component due to deprotonation of N(1)]. In [$TlMe_2$(Td)], O,S-coordination is still evidenced by the behaviour of $\nu(C{=}O)$, $\nu(C{=}S)$, $\nu(Tl{-}O)$ and $\nu(Tl{-}S)$, the latter two of which, like δ_{sym} (CH_3) and $\rho(CH_3)$, appear close to their positions in $[TlMe_2(BTd)]$; N-coordination is not evident. To sum up, whereas all three thallium compounds exhibit O, S-coordination, N-coordination is clearly present in $[TlMe_2(BTd)]$ but IR data are not conclusive for $[TlMe_2(Td)]$ or $[TlPh_2(Td)]$.

In the mercury compounds the shift to lower wavenumber and/or weakening or disappearance of $\nu(C{=}S)$ are indicative, as in related compounds,[1d,15] of S-coordination and considerable evolution from the thione to the thiol form. The $\nu(C{-}N{-}C)$ band located near 1300 or $1250\,cm^{-1}$ shifts slightly at most, but all such shifts are to higher wavenumbers, and may be indicative of N-coordination. As in the thallium compounds, the shift of $\nu(C{=}O)$ to lower wavenumbers upon-coordination is smaller for BTd than for Td but whereas this shift is greater than $40\,cm^{-1}$ in all the Tl complexes, in the case of the Hg-BTd compounds its small extent (14–$25\,cm^{-1}$) suggests that it may be just a consequence of deprotonation, S-coordination and subsequent electronic reordering rather than the result of O-coordination.[15b] The positions found for $\nu_{sym}(CH_3)$, $\rho(CH_3)$, $\nu(Hg{-}C)$ in the methyl derivatives, and for $\nu(Hg{-}S)$ and the t-mode of $\nu(Hg{-}C)$ in the phenyl derivatives are close to those found in systems in which the presence of a primary Hg–S bond together with other interactions has been proven crystallographically.[15]

Solution Studies

Due to the poor solubility of the complexes in non-polar solvents, all solution studies were carried out in DMSO. The molar conductivity (Λ_M) data (see Experimental Part) indicate that the $TlMe_2^+$ compounds are the most ionogenic, with Λ_M values of 18.8 and $13.1\,S\,cm^2\,mol^{-1}$ (the lower limit for 1 : 1 electrolytes is $22\,S\,cm^2\,mol^{-1}$),[16] $[TlPh_2(Td)]$ is less so $\Lambda_M = 5.6\,S\,cm^2\,mol^{-1}$) and the mercury compounds ($\Lambda_M = 0.2$ and $0.3\,S\,cm^2 mol^{-1}$) are clearly non-ionogenic in this medium.

The NMR data of thiohydantoin and its organometallic derivatives are summarized in Table III, in which the ligand signals have been assigned following Carlan *et al.*[17] The presence in the spectra of the complexes of just a single peak attributable to an N–H group indicates deprotonation of the ligand upon metallation; the breadth of this signal suggests proton exchange between N(1) and N(3) in this solvent. The C(5)–H signal is slightly shielded in the complexes and the fact that this shielding is considerably more intense for the $TlPh_2^+$ derivative than for the others may reflect the possible

TABLE III ^{1}H, ^{13}C, ^{199}Hg and ^{205}Tl NMR data[a] for HTd and its HgR and TlR_2 complexes (R = Me and/or Ph)

Compound	N(3)H	N(1)H	C(5)H	MR_n	$^{2}J(^{1}H{-}M)$	C(2)	C(4)	C(5)	MR_n	$^{1}J(^{13}C{-}M)$	M(W1/2)
HTd	11.68s	9.88s	4.09s			183.6	174.7	50.4			
[HgMe(Td)]	10.12sb		3.98s	0.72s	197.6	181.2	185.9	53.7	4.2	1521	– 830(552)
[HgPh(Td)]	10.35sb		4.05s	Ho 7.42d Hm 7.33t Hp 7.22t		179.8		53.3	Ci 152.8 Co 137.2 Cm 128.4 Cp 128.1		– 1167(1029)
[$TlMe_2$(Td)]			4.06s	0.85db							
[$TlPh_2$(Td)]	9.31sb		3.81s	Ho 7.48d Hm 7.43t Hp 7.29t		192.6	184.0	51.8	139.1 – 125.0		3125(7777)

[a] δ in ppm; Referenced to: TMS for ^{1}H and ^{13}C, neat $HgMe_2$ for ^{199}Hg and an infinitely diluted aqueous solution of $TlClO_4$ for ^{205}Tl. J in Hz; s = singlet; sb = singlet broad; d = doublet; db = doublet broad.

difference in coordination mode between the thallium and mercury compounds that is discussed below.

More precise evidence concerning coordination mode is provided by the ^{13}C data. While in the organomercury derivatives C(2) is more shielded than in the free ligand, as would be the result of evolution to the thiolic form upon complexation,[1d] in the thallium compound (the poor solubility of [$TlMe_2$(Td)] precluded recording of a ^{13}C NMR spectrum) the appearance of the C(2) signal at lower field than in the free ligand is indicative, as in [$TlPh_2$(Rd)],[1d] of poor evolution towards the thiol form. This in turn suggests greater Tl–O interaction.[1d] The fact that the downfield shifts of the C(4) and C(5) signals are smaller in the thallium compound is in keeping with this conclusion and the increase in the double bond character of the C–N linkage that follows coordination through the sulphur atom.[17]

Coordination to Hg *via* S and N appears to be evidenced by the organomercury moiety ^{1}H and ^{13}C data, which are practically the same as for [$(HgR)_2$(Tu)] (R = Me and Ph).[15b] This conclusion is reinforced by the ^{199}Hg chemical shifts, which are very sensitive to the nature of the coordinating atom,[15b] and which for the HTd compounds lie between those found for [HgR(Tu)] (– 732.1 ppm (R = Me) and – 1072.7 ppm (R = Ph)), in which the coordinating atom is sulphur, and [HgR(TuSMe)] (–918.1 (R = Me) and –1258.0 (R = Ph)), in which HgR is bound to a nitrogen atom; they are very close to those found in [$(HgR)_2$(Tu)] (–856.0 (R = Me) and –1185.8 (R = Ph)), in which the mercury is bonded to both sulphur and nitrogen atoms.[15b] The position of the ^{205}Tl signal of [$TlPh_2$(Td)] at lower field than in the spectrum of [$TlPh_2$(Rd)][1d] suggest a slighly different dissociative equilibrium for both compounds.

NMR data for HBTd and its compounds (Table IV) were identified on the basis of the HTd data and those of HPyTd.[1g,19] In the ^{1}H spectrum of the ligand, N(1)H and N(3)H appear at lower field, and C(6)H at rather higher field than for HPyTd. The aromatic proton locations are unremarkable.

Deprotonation of the ligand upon complexation is confirmed by the appearance in the ^{1}H spectra of all the complexes of just a single broad low field signal that is assigned to N(3)H. Relative to the free ligand, this signal is shielded in all the compounds, but more so in [$TlMe_2$(BTd)] than in the mercury derivatives. Again, C(6)H is shielded relative to HBTd in [$TlMe_2$(BTd)] and slightly deshielded in the Hg compounds, and C(8)H and C(12)H are also more deshielded in the latter than in the thallium complex. All this, and the fact that the $TlMe_2^+$ proton signals are very similar to those previously reported for [$TlMe_2$(PyTd)],[1g] can be interpreted in keeping with the conductivity results as a consequence of [$TlMe_2$(BTd)] being largely

TABLE IV ^{1}H, ^{13}C, ^{199}Hg and ^{205}Tl NMR data[a] for HBTd and its $TlMe_2$, HgMe and HgPh complexes

Compound	N(3)H	N(1)H	C(6)H	C(8)H	C(9)H	C(10)H	C(11)H	C(12)H	MR_n	$^{2}J(^{1}H-M)$	
HBTd	12.39(1)s	12.16(1)s	6.48(1)s	7.76(1)d	7.40(1)d	7.39(1)m	7.40(1)d	7.76(1)d			
[$TlMe_2$(BTd)]	11.02(1)s,b		6.16(1)s	7.89(1)d	7.32(1)d	7.24(1)m	7.32(1)d	7.89(1)d	0.97(6)db	421.4	
[HgMe(BTd)]	11.59(1)s,b		6.51(1)s	8.07(1)d	7.35(1)d	7.35(1)m	7.35(1)d	8.07(1)d	0.86(3)s	194.1	
[HgPh(BTd)]	11.68(1)s,b		6.51(1)s	8.08(1)	7.21(1)m	7.21(1)m	7.21(1)m	8.08(1)d	Ho 7.54(2)d		
									Hm 7.41(2)t		
									Hp 7.15(1)t		
	C(2)	C(4)	C(5)	C(6)	C(7)	C(8),C(12)	C(9),C(11)	C(10)	$M-CH_3$	$^{n}J(^{13}C-M)$	M(W1/2)
HBTd	179.5	166.0	128.0	111.6	132.5	130.2	128.8	129.1			
[$TlMe_2$(BTd)]	180.6	171.2	139.8	110.4	135.6	129.9	128.4	127.4	25.2db		2929 3499(1709)
[HgMe(BTd)]	170.8	170.1	140.0	117.4	134.8	131.0	128.5	128.9	7.7	1497	− 720.5
[HgPh(BTd)]	170.9	170.0	140.0	117.6	134.7	131.1	128.5	128.9	Ci 154.4		− 1062.2
									Co 137.0	111	
									Cm 128.3	200.0	
									Cp 128.0		

[a] δ in ppm; Referenced to: TMS for ^{1}H and ^{13}C, neat $HgMe_2$ for ^{199}Hg and an infinitely diluted aqueous solution of $TlClO_4$ for ^{205}Tl; J in Hz; s = singlet; sb = singlet broad; d = doublet; db = doublet broad; t = triplet; m = multiplet.

dissociated in DMSO whereas the organomercury derivates are largely non-dissociated. The ionization of $[\mathrm{TlMe_2(BTd)}]$ may likewise be held responsible for Tl/Hg ^{13}C differences, and is corroborated by the ^{13}C and ^{205}Tl $\mathrm{TlMe_2^+}$ data, which are very similar to those of other ionized $\mathrm{TlMe_2^+}$ compounds $[\mathrm{TlMe_2(PyTd)}]$[2], ($[\mathrm{TlMe_2(DABRd)}]$,[1g] $[\mathrm{TlMe_2(Rd)}]$[1d] and $\mathrm{TlMe_2ClO_4}$.[18]

In the organomercury derivatives, evolution of the ligand to the thiolic form shields C(2) more than in the Td compounds and the reorganization of charge in the five membered ring deshields C(4), C(5) and C(6). The ^{13}C chemical shifts of the organometallic moieties, are similar to those found in [HgMe(HTu)][15b] and [HgPh(HTu)],[15b] in which Hg is only coordinated by a sulphur atom. The fact the ^1J value of [HgMe(BTd)] is smaller than those of [HgMe(Td)] and [HgMe(TuSMe)],[15b] which are N, S-coordinated, likewise points to the [HgR(BTd)] species being essentially S-bonded. This conclusion is reinforced by the ^{199}Hg chemical shifts, which show the Hg nucleus to be only slightly less shielded than in [HgMe(HTu)] (− 732.1 ppm) and [HgPh(Htu)] (−1072.7 ppm), and clearly less shielded in [HgPh(BTd)] than in [HgPh(PyTd)] (−1173 ppm), which is S, N-coordinated.[19]

Supplementary Material

Lists of H atom positions, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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