

Diphenylthallium(III) thiosemicarbazones: flexibility of coordination in the solid state and polymorphism in chloroform solution

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Dedicated in honor of Professor R. Usón

Abstract

The reactions of diphenylthallium(III) hydroxide in water–ethanol at room temperature with thiosemicarbazones $HL = R = N(3)-N(2)H-C(1)(S)-N(1)H_2$ ($RO =$ cyclopentanone, benzaldehyde, 2-hydroxybenzaldehyde, 4-methoxybenzaldehyde, acetophenone, furan-2-carbaldehyde, pyridine-2-formaldehyde and pyridine-2-acetaldehyde) afforded novel diphenylthallium(III) thiosemicarbazones of stoichiometry $[TlPh_2(L)]$ (compounds **1–8**, respectively) that were characterised with the help of analytical data, physical properties, IR spectrometry, multinuclear (1H , ^{13}C and ^{205}Tl) NMR spectroscopy and X-ray studies of **1**, **7** and **8**. In crystals of **1** (and probably also in those of **2**, **4**, **5** and **6**), $Tl(III)$ is bound to two phenyl carbons and to the $N(3)$ and S atoms of the monodeprotonated thiosemicarbazone in a distorted trigonal bipyramidal coordination polyhedron with one vacant site in the equatorial plane. In **3** the metal atom is $S,N(3),O$ -coordinated. In **7** and **8** there are three independent molecules: all three have distorted trigonal bipyramidal coordination with Tl coordinated to two carbon atoms and to the $N(Py)$, $N(3)$ and S atoms of the deprotonated thiosemicarbazones, but they differ significantly in their bonding parameters. The ^{205}Tl NMR spectra suggest that for **1–6** more than one coordination mode is present in solution in chloroform, whereas for **7** and **8** there is only one species. Low temperature proton NMR studies of **7** and **8** showed that the energy barrier to rotation of the amino groups about the C^1-N^1 bond correlated with the bonding parameters of the thioamide group in the solid state; in both cases the barrier is somewhat higher than in thiosemicarbazones of $PhHg(II)$.

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1. Introduction

There are several reasons for interest in the coordination chemistry of thiosemicarbazones [1–5]. In particular, metal derivatives of thiosemicarbazones often display better pharmacological properties than the thiosemicarbazones themselves; and as a class, metal–thiosemicarbazone complexes exhibit a great variety of

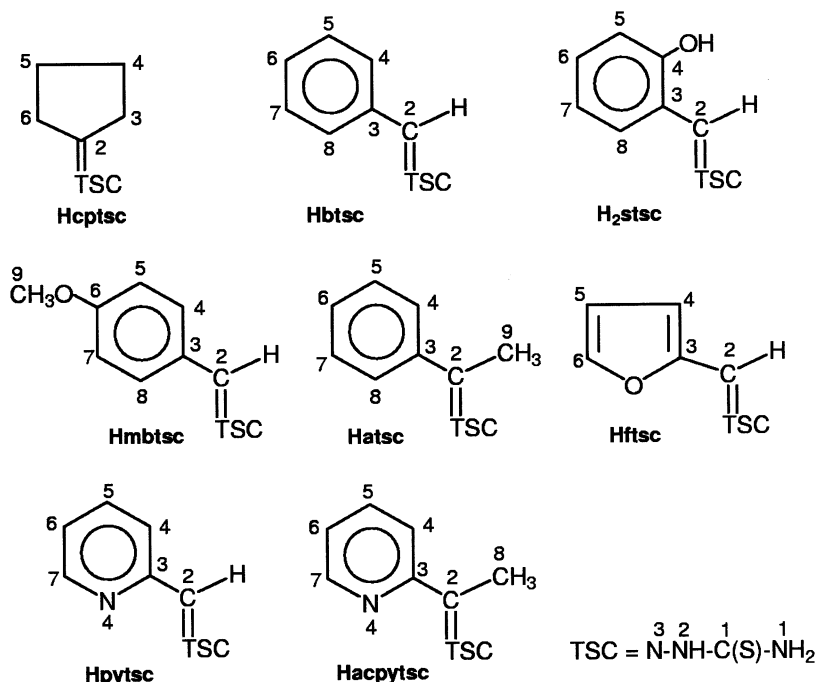
coordination modes and structures [1–4]. Because of their biological importance, complexes of thiosemicarbazones with transition metals have been more intensively investigated than their complexes with main group elements [1–5]. However, interest in thiosemicarbazones of organometallic cations with heavy metals M has increased in relation with efforts to activate $M-C$ bonds by coordination so as to convert toxic organometallic substrates into less toxic inorganic compounds [6–11].

We recently reported a series of thiosemicarbazones of organomercury(II) cations RHg^+ ($R = C_6H_5-$ or $2-C_5H_4NC_6H_4-$) [12,13]. Here we describe analogous thiosemicarbazones of diphenylthallium(III) cation, Ph_2Tl^+ (Scheme 1 shows the parent thiosemicarba-

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Scheme 1.

zones). In most of the few organothallium(III) thiosemicarbazones reported previously the cation is Me_2Tl^+ [5]. We found the new diphenylthallium(III) thiosemicarbazones to have interesting bonding properties, both in the solid state and in CDCl_3 solution.

2. Experimental

2.1. General materials

Cyclopentanone, benzaldehyde, salicylaldehyde, *p*-methoxybenzaldehyde, acetophenone, 2-furaldehyde, 2-pyridineacetaldehyde, 2-pyridineacetaldehyde, thiosemicarbazide, thallium(I) bromide and phenylboronic acid were of reagent grade and were used without further purification.

2.2. Synthesis of TlPh_2X ($\text{X} = \text{OH}, \text{Br}$) and ligands

Diphenylthallium(III) hydroxide was prepared by a method used previously [14] for dimethylthallium(III) hydroxide, by stirring diphenylthallium(III) bromide for 24 h at room temperature (r.t.) with a freshly prepared aqueous suspension of Ag_2O [from AgNO_3 (0.8 g) and NaOH (1.5 g) in H_2O], followed by filtration. TlPh_2Br was prepared as follows [15]: bromine (1.5 ml) was added with stirring to a suspension of solid thallium(I) bromide (6.25 g) in water (30 ml) until formation of a clear solution that, following removal of excess bromine under vacuum, was slowly added to a suspension of

phenylboronic acid (6.0 g) in water (20 ml); this mixture was refluxed for 5 h and allowed to cool, and the TlPh_2Br formed was filtered out, washed with water and dried in vacuo.

Caution! thallium is a highly toxic cumulative poison and thallium compounds should be handled carefully.

The ligands were prepared following a published [16] general procedure by reacting the thiosemicarbazide with the corresponding aldehyde or ketone in ethanol/water. The properties of most of the ligands used, and other relevant details, have been described elsewhere [12].

2.3. Synthesis of the complexes

2.3.1. $[\text{TlPh}_2(\text{cptsc})]$ (I)

A solution of $\text{TlPh}_2(\text{OH})$ (0.260 g, 0.73 mmol) in water (40 ml) was added slowly with stirring to a solution of Hcptsc (0.115 g, 0.73 mmol) in ethanol (25 ml). The mixture was stirred for 36 h at r.t. (ca. 25 °C) and the volume was reduced when a white solid started forming. The solid was recrystallised from chloroform–ethanol and dried in vacuo. Yield, 45%; m.p., 150–155 °C (decomp.). *Anal.* Found: C, 41.1; H, 3.99; N, 8.97. Calc. for $\text{C}_{18}\text{H}_{20}\text{TlN}_3\text{S}$: C, 41.9; H, 3.88; N, 8.16%. IR spectrum (cm^{-1}): 3454s, 3335s, $\nu(\text{NH}_2)$; 1591s, $\nu(\text{CN})$; 790w, $\nu(\text{CS})$; 242, $\nu(\text{TIC})$. Crystals suitable for the X-ray study were grown from ethanol.

2.3.2. [TIPh₂(btsc)] (2)

A solution of TIPh₂(OH) (0.430 g, 1.14 mmol) in water (40 ml) was added slowly with stirring to a solution of Hbtsc (0.205 g, 1.14 mmol) in ethanol (25 ml). The mixture was stirred for 48 h at r.t. (ca. 25 °C) and the light green solid formed was filtered out, washed with ethanol, recrystallised from chloroform–ethanol and dried in vacuo. Yield, 40%; m.p., 140–145 °C (decomp.). *Anal.* Found: C, 44.1; H, 3.30; N, 7.82. Calc. for C₂₀H₁₈TiN₃S: C, 44.7; H, 3.35; N, 7.82%. IR spectrum (cm⁻¹): 3491m, 3372m, ν(NH₂); 1568vs, ν(CN); 805m, ν(CS); 250m, ν(TiC).

2.3.3. [TIPh₂(Hstsc)] (3)

A solution of TIPh₂(OH) (0.430 g, 1.14 mmol) in water (40 ml) was added slowly with stirring to a solution of H₂stsc (0.225 g, 1.14 mmol) in ethanol (25 ml). The mixture was stirred for 40 h at r.t. (ca. 25 °C), and the light-green solid formed was filtered out, washed with ethanol, recrystallised from chloroform–ethanol and dried in vacuo. Yield, 40%; m.p., 118–130 °C (decomp.). *Anal.* Found: C, 42.7; H, 2.92; N, 7.64. Calc. for C₂₀H₁₈TiN₃SO: C, 43.4; H, 3.25; N, 7.59%. IR spectrum (cm⁻¹): 3443m,br, 3330m,br, ν(NH₂); 1594s, ν(CN); 1303s, ν(CO); 816w, ν(CS); 246m, ν(TiC).

2.3.4. [TIPh₂(mbtsc)] (4)

A solution of TIPh₂(OH) (0.260 g, 0.73 mmol) in water (40 ml) was slowly added with stirring to a solution of Hmbtsc (0.145 g, 0.73 mmol) in ethanol (25 ml). The mixture was stirred for 40 h at r.t. (ca. 25 °C), and the white solid formed was filtered out, washed with ethanol, recrystallised from chloroform–ethanol and dried in vacuo. Yield, 72%; m.p., 125–140 °C (decomp.). *Anal.* Found: C, 43.4; H, 3.46; N, 7.25. Calc. for C₂₁H₂₀TiN₃SO: C, 44.4; H, 3.53; N, 7.40%. IR spectrum (cm⁻¹): 3498m, 3373m, ν(NH₂); 1571s, ν(CN); 1247s, ν(CO); 809m, ν(CS); 252m, ν(TiC).

2.3.5. [TIPh₂(atasc)] (5)

A solution of TIPh₂(OH) (0.260 g, 0.73 mmol) in water (40 ml) was added slowly with stirring to a solution of Hatasc (0.135 g, 0.73 mmol) in ethanol (25 ml). The mixture was stirred for 24 h at r.t. (ca. 25 °C), and the light steel grey solid formed was filtered out, washed with ethanol, recrystallised from chloroform–ethanol and dried in vacuo. Yield, 52%; m.p., 130–140 °C (decomp.). *Anal.* Found: C, 45.7; H, 3.56; N, 7.61. Calc. for C₂₁H₂₀TiN₃S: C, 45.7; H, 3.63; N, 7.62%. IR spectrum (cm⁻¹): 3485s, 3353s, ν(NH₂); 1566vs, ν(CN); 818m, ν(CS); 244, ν(TiC).

2.3.6. [TIPh₂(ftsc)] (6)

A solution of TIPh₂(OH) (0.260 g, 0.73 mmol) in water (40 ml) was added slowly with stirring to a solution of Hftsc (0.116 g, 0.73 mmol) in ethanol (25 ml). The mixture was stirred for 48 h at r.t. (ca. 25 °C) and the light steel grey solid formed was filtered, washed with ethanol, recrystallised from chloroform–ethanol and dried in vacuo. Yield, 43%; m.p., 145–155 °C (decomp.). *Anal.* Found: C, 40.4; H, 2.88; N, 7.85. Calc. for C₁₈H₁₆TiN₃SO: C, 41.0; H, 3.04; N, 7.97%. IR spectrum (cm⁻¹): 3479m, 3438m, 3350m, ν(NH₂); 1588s, ν(CN); 809m, ν(CS); 247m, ν(TiC).

2.3.7. [TIPh₂(pytsc)] (7)

A solution of TIPh₂(OH) (0.345 g, 0.92 mmol) in water (40 ml) was added slowly with stirring to a solution of Hpytsc (0.167 g, 0.92 mmol) in ethanol (25 ml). The mixture was stirred for 30 h at r.t. (ca. 25 °C), and the light greenish-yellow solid formed was filtered out, washed with ethanol, recrystallised from ethanol and dried in vacuo. Yield, 46%; m.p., 170–180 °C (decomp.). *Anal.* Found: C, 42.2; H, 3.22; N, 10.45. Calc. for C₁₉H₁₇TiN₄S: C, 42.4; H, 3.16; N, 10.41%. IR spectrum (cm⁻¹): 3470m, 3435m, 3310sh, 3262m, ν(NH₂); 1588s, ν(CN); 790m, ν(CS); 619m, δ(CH)_{o,p.}; 427m, δ(CH)_{i,p.}; 246m, ν(TiC). Crystals suitable for the X-ray study were grown from chloroform–ethanol.

2.3.8. [TIPh₂(acpytsc)] (8)

A solution of TIPh₂(OH) (0.260 g, 0.73 mmol) in water (40 ml) was slowly added with stirring to a solution of Hacpytsc (0.135 g, 0.73 mmol) in ethanol (25 ml). The mixture was stirred for 24 h at r.t. (ca. 25 °C), its volume was reduced under vacuum, and the light greenish–yellow solid formed was filtered out, washed with ethanol, recrystallised from ethanol and dried in vacuo. Yield, 50%; m.p., 150–155 °C (decomp.). *Anal.* Found: C, 42.9; H, 3.13; N, 9.94. Calc. for C₂₀H₁₉TiN₄S: C, 43.5; H, 3.44; N, 10.14%. IR spectrum (cm⁻¹): 3450m, 3430m, 3312m,br, ν(NH₂); 1586s, ν(CN); 798m, ν(CS); 628m, δ(CH)_{o,p.}; 424m, δ(CH)_{i,p.}; 249m, ν(TiC). Crystals suitable for the X-ray study were grown from chloroform–ethanol.

2.4. Physical measurements

Elemental analyses for C, H and N were performed with a Carlo–Erba 1108 microanalyser. Melting points were determined with a Gallenkamp electrically heated apparatus. Infrared spectra were recorded with samples in KBr pellets (4000–400cm⁻¹) or in Nujol mulls between polyethylene sheets (500–100 cm⁻¹) on a Bruker IFS 66 V spectrometer. NMR spectra were recorded with samples in CDCl₃ using a Bruker AMX 300 spectrometer at 300.14 and 75.48 MHz for ¹H and ¹³C spectra, respectively (both with TMS as internal

Table 1
Summary of crystal data for compounds **1**, **7** and **8**

	[TlPh ₂ (cptsc)] (1)	[TlPh ₂ (pytsc)] (7)	[TlPh ₂ (acpytsc)] (8)
Chemical formula	C ₁₈ H ₂₀ TlN ₃ S	C ₁₉ H ₁₇ TlN ₄ S	C ₂₀ H ₁₉ TlN ₄ S
Formula weight	514.80	537.80	551.82
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)
Unit cell dimensions			
<i>a</i> (Å)	9.5659(10)	13.489(5)	12.357(2)
<i>b</i> (Å)	12.139(2)	15.178(6)	12.787(2)
<i>c</i> (Å)	16.388(2)	15.682(3)	19.600(2)
α (°)		71.038(19)	81.022(10)
β (°)	106.318(11)	69.435(18)	86.585(10)
γ (°)		82.25(4)	77.345(10)
<i>U</i> (Å ³)	1826.3(4)	2842.3(16)	2983.7(7)
<i>Z</i>	4	6	6
μ (Mo Kα) (mm ⁻¹)	8.960	8.642	8.235
No. of reflections collected	3843	14860	12671
No. of unique reflections/R _{int}	3710/0.0286	14351/0.0821	12088/0.0333
No. of observed reflections	3710	6087	7965
Final R ₁ [<i>I</i> > 2σ(<i>I</i>)]/wR ₂	0.0305/0.0655	0.0472/0.0746	0.0341/0.0700

reference) and at 173.76 MHz for ²⁰⁵Tl spectra (using an aqueous solution of TlClO₄ extrapolated to infinite dilution as external reference). All physical measurements were carried out in the RIAIDT services of the University of Santiago de Compostela.

2.5. Structure determinations

Suitable crystals of **1**, **7** and **8** were mounted on an Enraf–Nonius MACH3 automatic diffractometer [17a]. Data were collected at 293 K by the ω–2θ scan technique using Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects [17b]. Empirical [17c] absorption corrections were applied for **1** and **8** and a semi-empirical correction (psi scan) [17d] for **7**. Structures **1** and **8** were solved by the heavy atom method [17e] and **7** by direct methods [17f]. All three were refined by full-matrix least-squares methods based on *F*². All non-hydrogen atoms were refined anisotropically [17g]. Hydrogen atoms were included in the model at geometrically calculated positions. Atomic scattering factors were taken from International Tables for Crystallography [17h]. Molecular graphics were generated with ORTEP [17i].

Crystal data, experimental details and refinement results are listed in Table 1.

3. Results and discussion

3.1. General comments

The reactions of diphenylthallium(III) hydroxide at room temperature with the thiosemicarbazones HL of

Scheme 1 afforded diphenylthallium(III) thiosemicarbazonates [TlPh₂(L)]. The spectral data suggest that the most acidic group of HL, –N(2)H, is deprotonated in all these complexes except in **3**.

The new compounds are white, light steel grey, pale-green or light greenish yellow (cf. experimental), and rather than melting decompose to black material at temperatures in the range 118–180 °C. They are stable to light and moisture in the solid state, but decompose in solution if left for 3 days or more. All are soluble in DMSO; **2**, **4**, **5**, **6** and **8** are completely soluble in dichloromethane and chloroform and slightly soluble in ethanol and methanol; **1** and **3** are partially soluble in these four solvents; and **7** is soluble in all the solvents.

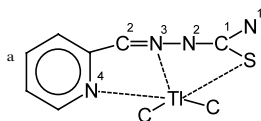
3.2. Crystal and molecular structures

The crystal data and most significant bond lengths and angles of **1**, **7** and **8** are listed in Tables 1 and 2, respectively, and [TlPh₂(cptsc)] (**1**) and [TlPh₂(pytsc)] (**7**, molecule 1) are shown together with their atom numbering schemes in Figs. 1 and 2, respectively. In all three compounds the ligand adopts *Z*-configuration with respect to the N(2)–C(1) bond, chelating the Tl atom via N(3) and S (in **1**) or N(4), N(3) and S (in **7** and **8**). Whereas **1** has only one form of the molecule in its crystal lattice, the crystals of **7** and **8** both have three independent molecules differing significantly in their bonding parameters. Packing in the lattice appears to stabilize the independent molecules, because in solution only one species was detected by NMR (vide infra).

In compound **1**, Tl(III) is bound to one carbon atom of each of the phenyl groups [C(7) and C(13)] and to the donor atoms [(N(3) and S)] of the deprotonated

Table 2
Some significant bond lengths (Å) and bond angles (°) in compounds **1**, **7** and **8**

Parameter ^a	Compound	Molecule 1	Molecule 2	Molecule 3
<i>Bond lengths</i>				
Tl–N(3)	1	2.452(5)		
	7	2.547(7)	2.472(7)	2.537(7)
	8	2.500(6)	2.558(5)	2.485(5)
Tl–S	1	2.6156(18)		
	7	2.779(3)	2.691(3)	2.764(3)
	8	2.711(2)	2.7339(19)	2.743(2)
Tl–N(4)	7	2.657(7)	2.708(8)	2.641(8)
	8	2.569(6)	2.613(5)	2.644(6)
Tl–C	1	2.146(6)		
		2.148(6)		
	7	2.154(9)	2.156(9)	2.161(9)
		2.141(9)	2.139(10)	2.140(9)
	8	2.175(7)	2.150(7)	2.146(8)
S–C(1)	1	1.749(7)		
	7	1.724(9)	1.711(9)	1.724(11)
	8	1.727(9)	1.729(7)	1.742(7)
C(1)–N(1)	1	1.344(8)		
	7	1.317(10)	1.339(10)	1.357(11)
	8	1.353(9)	1.353(8)	1.350(9)
C(1)–N(2)	1	1.302(8)		
	7	1.321(10)	1.331(10)	1.299(11)
	8	1.295(9)	1.310(8)	1.290(9)
N(2)–N(3)	1	1.391(7)		
	7	1.383(9)	1.392(9)	1.361(9)
	8	1.382(8)	1.392(7)	1.368(7)
C(2)–N(3)	1	1.278(7)		
	7	1.258(10)	1.288(10)	1.266(11)
	8	1.281(8)	1.299(8)	1.304(8)
<i>Bond angles</i>				
C–Tl–C	1	146.6(2)		
	7	160.6(3)	154.7(4)	158.2(4)
	8	151.1(3)	157.7(3)	152.8(3)
N(3)–Tl–S	1	72.90(12)		
	7	68.39(18)	71.60(18)	68.97(19)
	8	70.88(13)	69.51(12)	71.29(14)



cyclopentanone thiosemicarbazone (cptsc⁻). The Tl–N(3) bond length, 2.452(5) Å, is shorter than in [TlMe₂(cptsc)], in which Tl–N(3) = 2.55(1) Å [18], and so is the Tl–S distance though less markedly {**1**, 2.6156(18); [TlMe₂(cptsc)], 2.627(5) Å}. This shortening of the Tl–N(3) and Tl–S bonds is accompanied by a lengthening of the Tl–C distances, 2.146(6) and 2.148(6) Å in **1** as against 2.07(3) and 2.13(3) Å in [TlMe₂(cptsc)]. The Tl–N and Tl–S bonds in **1** are also shorter than those of [TlMe₂(mbtsc)] [19], in which mbtsc⁻ is bound to Tl via N(2) and S instead of N(3) and S [with Tl–N(2) = 2.56(1) Å and Tl–S = 2.991(4) Å], and those of other diorganothallium(III) compounds [10,14,20–22].

The C–S bond length, 1.749(7) Å, is shorter than a single bond ($d_{C-S} = 1.81$ Å) but longer than a C=S double bond ($d_{C-S} = 1.62$ Å) [23], suggesting partial double bond character. Interestingly, the length of this bond in [TlMe₂(cptsc)], 1.78(2) Å [18,23], is close to that of a single bond even though the Tl–S bond is also slightly longer than in **1**; this is probably due to the S atom of [TlMe₂(cptsc)] being involved in a weak additional Tl···S interaction that is not present in **1**. The C(2)–N(3) bond length, 1.278(7) Å, is that of a double bond ($d_{C=N} = 1.28$ Å) [23], and the deprotonation of –N(2)H lends C(1)–N(2) double bond character, shortening it to 1.302(8) Å {close to the length of a C–N double bond and somewhat shorter than the 1.310(2) Å of [TlMe₂(cptsc)]}. The thiosemicarbazone bite angle N(3)–Tl–S, 72.90(12)°, is close to that of [TlMe₂(cptsc)], 70.9(3)° [18]. These and other bond angles allow the coordination polyhedron to be described as a distorted trigonal bipyramid with one vacant equatorial position.

The crystal and molecular structures of compounds **7** and **8** are similar. Both compounds crystallize in the same space group and both have three independent molecules in the asymmetric unit. The closest precedent for such variety is [TlMe₂(pytsc)], in which there are two independent molecules in each asymmetric unit [24]. For clarity, Fig. 2 shows only molecule **1** of compound **7**; compound **8** is very similar and is not shown. Table 2 lists the most significant bond lengths and angles of the three molecules of each compound. In general, the Tl–N(3) bonds in **7** and **8** are shorter than in [TlMe₂(pytsc)], as are Tl–S and Tl–N(4); however, the Tl–C bonds are clearly longer in the diphenylthallium derivatives. The bite angle N(3)–Tl–S is wider in **7** and **8** than in [TlMe₂(pytsc)], but the C–Tl–C bond angle is narrower. As expected, the pentacoordinated Tl of **7** and **8** has longer Tl–N(3) and Tl–S bonds than the tetra-coordinated Tl of **1**.

In keeping with the general tendency of diorganothallium(III) compounds to acquire high coordination number by binding to donor atoms of a second molecule [18,19], the Tl of molecule **1** of **7** interacts weakly with S(1)ⁱ ($i = 1-x, 2-y, -z$; Tl(1)···S(1)ⁱ = 3.425(3) Å, sum of the van der Waals radii 3.76 Å [23]), giving rise to a very weakly bound dimer. Molecule 3 of compound **8** has a similar but even weaker interaction [Tl(3)···S(3)ⁱ = 3.614(2) Å, $i = -x, 2-y, 1-z$]. These two bonds are shorter than the analogous bond of molecule 1 of [TlMe₂(pytsc)] [3.671(2) Å], but longer than that of molecule 2 [3.207(3) Å] [24].

In all three compounds (**1**, **7** and **8**) a hydrogen bond network stabilizes the lattice (see Table 3). In **1**, a weak intermolecular hydrogen bond between N(1)–H(1B) and the S atom of a neighboring molecule links the molecules in dimers. In **7** there are three hydrogen bonds, two binding molecule **1** to molecules **2** and **3**, and one between two molecules of type **2**; no S atoms are

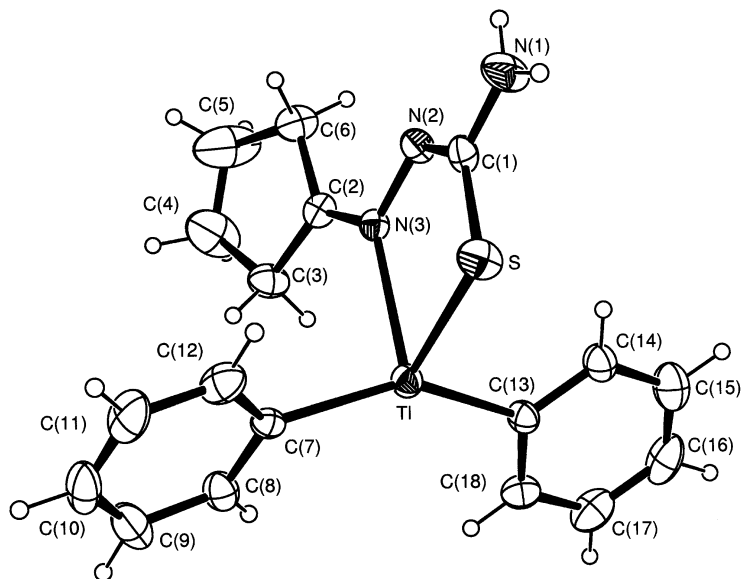


Fig. 1. An ORTEP drawing of $[\text{TIPh}_2(\text{cptsc})]$ (**1**), showing the molecular structure and the labelling scheme.

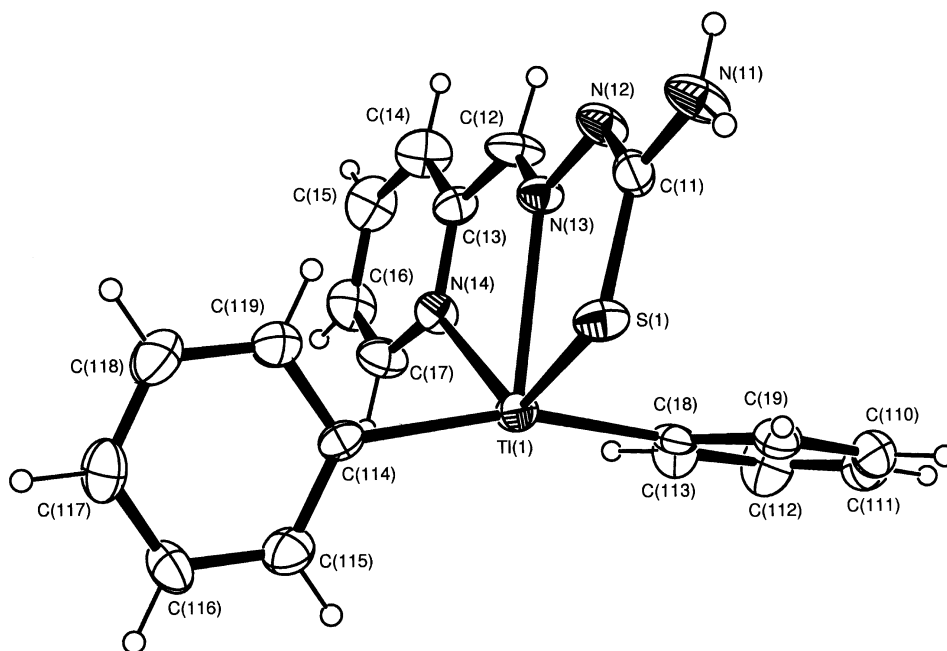


Fig. 2. An ORTEP drawing of molecule **1** of $[\text{TIPh}_2(\text{pytscc})]$ (**7**), showing the molecular structure and the labelling scheme.

involved in any of the three. There are also three hydrogen bonds in **8**, two of them binding molecule **1** to molecule **3** via S atoms, and one between two molecules of type **2**.

3.3. IR spectra

The main IR bands of the complexes are listed in the Experimental part. For discussion of these spectra the complexes can be grouped in two classes: those in which there is no donor atom in the R substituent of the

thiosemicarbazone ligand (**1**, **2** and **5**), and those in which there is (**3**, **4**, **6**, **7** and **8**).

Analysis of the shifts that the free thiosemicarbazone IR bands undergo upon deprotonation and coordination suggests that in the first class **2** and **5** have the same N(3),S-coordination as was found in the X-ray study of **1**. As in the spectra of other complexes of deprotonated thiosemicarbazones [12], the $\nu[\text{N}(2)\text{H}]$ band located around 3100 cm^{-1} in that of the free ligand disappears (although a weak residual band in the spectrum of **1** suggests that in Hcptsc this is a multicomponent band).

The $\nu(\text{NH}_2)$ bands are slightly shifted to higher wavenumbers, indicating that this group is not coordinated to Tl. The coordination of N(3) does not shift $\nu(\text{CN})$ significantly, but coordination of S shifts the $\nu(\text{CS})$ band located between 830 and 820 cm^{-1} to lower wavenumbers, and bands between 1100 and 1000 cm^{-1} are weakened.

For the compounds with a donor atom in the R substituent of the ligand, spectral changes similar to those described above likewise show coordination via N(3) and S. In the spectra of **7** and **8**, coordination by the pyridine N is reflected by the shift to higher wavenumbers of the in-plane and out-of-plane CH vibrations. In the spectra of **4** and **6** $\nu(\text{C}-\text{O})$ and the furan ring vibrations, respectively, are practically in the same positions as in those of the free ligands, which argues against O-coordination.

In the spectrum of **3**, broad bands at 3443 and 3330 cm^{-1} are attributed to $\nu(\text{NH}_2)$. A medium intensity band at 3146 cm^{-1} might in principle be due to either $\nu(\text{OH})$ or $\nu(\text{NH})$ depending on the location of the H atom remaining after monodeprotonation, but attribution to $\nu(\text{NH})$ seems more plausible in view of the O-coordination suggested by the shift of the $\nu(\text{CO})$ bands (at 1283s and 1267s in the free ligand) to higher wavenumbers close to their positions in the spectra of complexes in which this ligand is S,N,O-coordinated and bideprotonated [25]. This probable S,N(3),O-coordination of **3** contrasts with the essentially monodentate S-donor behaviour found [13] in the [2-(pyridin)-2'-yl]phenyl]mercury(II) complex of this ligand, in which, as in **3**, it is monodeprotonated.

Finally, whether the metal is tetra-, penta- or hexacoordinated does not significantly affect the position of $\nu(\text{Tl}-\text{C})$, which in all cases appears as a band close to 250 cm^{-1} .

3.4. Solution-phase studies

3.4.1. ^1H and ^{13}C NMR spectra

The chief ^1H NMR data for the complexes in CDCl_3 are listed in Table 4. In general, the spectra show more than one signal associated with each resonant nucleus

(only the most intense signal is listed in the tables). Deprotonation of N(2)H is shown by all of the complexes except **3** having any signal in the 8–12 ppm [13] region [compound **3** has a signal at 10.76 ppm, a position intermediate between the $-\text{OH}$ (9.87 ppm) and $-\text{N}(2)\text{H}$ (11.38) signals of free H_2stsc in DMSO-d_6] [13]. As usual, the NH_2 protons appear as single peaks (compounds **1**, **3** and **5–8**) or vanish (compounds **2** and **4**), whereas in the room temperature spectra of the free thiosemicarbazones they appear as two broad peaks in the region 6–9 ppm [12]. The *o*-, *m*- and *p*-Ph proton signals of Ph_2Tl^+ are separated by the ^{205}Tl nucleus ($I = 1/2$); the *o*-Ph signals have $^3J_{\text{Tl}-\text{H}}$ values of 400–450 Hz (Table 4), but due to the overlapping of signals it was only possible to calculate $^4J_{\text{Tl}-\text{H}}$ and $^5J_{\text{Tl}-\text{H}}$ for some of the compounds.

The ^{13}C NMR data are listed in Table 5. The interaction of diphenylthallium(III) with the thiosemicarbazones mainly affects C(1) and C(2) (see Refs. [12,26] for the data of the free ligands); Ph_2Tl^+ carbons remain unaffected, as do ligand ring carbons (except in **7** and **8**; vide infra). The accumulation of negative charge on the donor S atom, and the downfield shift of the C(2) signal relative to the free ligands, suggest that N(3),S-coordination holds in **1–6**. In **7** and **8** coordination affects the pyridyl signals as well as those of C(1) and C(2). C(3) and C(7) move upfield and C(4–6) move downfield relative to the free ligand in DMSO-d_6 [26]. Further, the $^1J_{\text{Tl}-\text{C}}$ coupling constants of **7** and **8** are the largest, followed by that of **6**. Coordination of the pyridyl group to Ph_2Tl^+ transfers additional charge to Tl, which in turn seems to pass it on to the phenyl groups, increasing the $^{13}\text{C}-^{205}\text{Tl}$ coupling. The $^3J_{\text{C}-\text{Tl}}$ values, involving *meta*-carbons, are also highest for **7** and **8**.

3.4.2. ^{205}Tl NMR spectra

Table 6 lists ^{205}Tl NMR data for **1–8**. All signals are rather narrow singlets. Complexes **7** and **8**, which contain pyridyl groups, showed only one signal each, in contrast to the two, three or even four signals shown by **1–6**. Most of the peaks occur in the regions 3728–3766 ppm (peak I), 3612–3662 ppm (peak II) and 3461–

Table 3
Intermolecular hydrogen bonds in compounds **1**, **7** and **8** (Å, °)

Compound	D–H···A	$d(\text{D}-\text{H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
1	N(1)–H(1)B···S ⁱ	0.86	2.70	3.512(6)	157.5
7	N(11)–H(11)B···N(32) ⁱⁱ	0.860	2.207	3.048	165.79
	N(21)–H(21)A···N(22) ⁱⁱⁱ	0.860	2.135	2.973	164.79
8	N(21)–H(21)B···N(12)	0.860	2.252	3.098	167.95
	N(11)–H(11)B···S(3) ^{iv}	0.860	2.734	3.575	166.48
	N(21)–H(21)A···N(22) ^v	0.860	2.322	3.085	147.97
	N(31)–H(31)B···S(1) ^{vi}	0.860	2.620	3.456	164.37

(i) $-x, -y+1, -z+1$, (ii) $-x+1, -y+2, -z+1$, (iii) $-x+1, -y+1, -z+1$, (iv) $x+1, y-1, z$, (v) $-x+2, -y+1, -z$, (vi) $x-1, y+1, z$.

Table 4
¹H NMR data (δ , ppm; J , Hz) for diphenylthallium(III) thiosemicabazonates

Compound	N(1)H ₂ /OH	C(2)H/C(2)- CH ₃	Ligand protons	TlPh ₂ protons		
				<i>o</i> -Ph (³ $J_{\text{Tl-H}}$)	<i>m</i> -Ph (⁴ $J_{\text{Tl-H}}$)	<i>p</i> -Ph (⁵ $J_{\text{Tl-H}}$)
[TlPh ₂ (cptsc)] (1)	5.02s		2.51t (C ^{3,6} H ₂), 2.20b (C ^{3,6} H ₂), 1.61m (C ^{4,5} H ₂)	7.71d (404)	7.44dt (120)	7.31d (46)
[TlPh ₂ (btsc)] (2)	^a	7.93s	7.20–7.6m (C ^{4–8} H)	7.75d (417)	^b	^b
[TlPh ₂ (Hstsc)] (3)	5.70s, 10.76s	8.01s	7.23td (C ⁶ H), 7.08dd (C ⁵ H), 6.94d (C ⁸ H), 6.83td (C ⁷ H)	7.79d (419)	~7.50d	^c
[TlPh ₂ (mbtsc)] (4)	^a	7.89s	7.54d (C ^{5,7} H), 6.85d (C ^{4,8} H), 3.81s (CH ₃)	7.77d (420)	~7.48d	~7.33
[TlPh ₂ (atsc)] (5)	5.18s	2.36s (CH ₃)	7.07–7.80(C ^{4–8} H)	^b	^b	^b
[TlPh ₂ (ftsc)] (6)	5.26s	8.13s	7.52d (C ⁶ H), 6.57d (C ⁴ H), 6.49dd (C ⁵ H)	7.69d (422)	7.40d (130)	~7.30
[TlPh ₂ (pytsc)] (7)	5.51s	8.43s	8.59s (C ⁷ H), 7.79t (C ⁵ H), 7.11s (C ⁶ H)	7.68d (450)	~7.34d	^d
[TlPh ₂ (acpytsc)] (8)	5.44s	2.54s (CH ₃)	8.56d (C ⁷ H), 7.83td (C ⁵ H), 7.66d (C ⁴ H), 7.10b (C ⁶ H)	7.62d (440)	7.32d (133)	7.30d (26)

^a Not observed.

^b Overlapping ligand ring signals.

^c One of the signals of this doublet appears at 7.44 ppm, the other overlaps ligand ring signals and the *m*-PhTl signals.

^d Overlapping ligand ring signals and the *m*-PhTl signals.

3498 ppm (peak III), although **3** and **5** each show an additional signal outside these ranges (Table 6). The presence of more than one signal in the spectra may be due either to association/dissociation equilibria or to coordination isomerism. Since **7** and **8** each show a single peak in the high field region (the location expected for Tl nuclei that are more shielded than in **1**, **2**, **4**, **5** and **6** due to their higher coordination numbers; vide supra), these phenomena probably do not affect these complexes, i.e. the N,N,S-coordination observed in the solid state (vide supra) remains in solution (indeed, even association via intermolecular Tl⋯S interactions cannot be completely ruled out). Note that it is no longer possible to distinguish three independent molecules as it is in the crystal; either there is only one species in chloroform or the three species do not differ enough to produce significantly distinct ²⁰⁵Tl signals.

The multiplicity of signals in **1–6** may be due partially to dissociation equilibria and partially to co-existence of complexes with different co-ordination modes (recall that the structure of [TlMe₂(mbtsc)] shows that N(2),S-coordination is possible as well as N(3),S-coordination in this type of complex) [19]. The presence of more than one coordination mode is supported by the fact that the complex with the greatest number of peaks (four) is **3**, which is probably O,N(3),S-coordinated in the solid state (vide supra) and which in CDCl₃ solution may also exist as O,N(3)-, N(3),S- and N(2),S-coordinated forms due to a prototropic –OH ↔ –N(2)H equilibrium. It must nevertheless be pointed out that many of the species reflected in Table 6 are only present in very low concentration. The absence of any polymorphism in solutions of **7** and **8** is possibly attributable to the very strong N,N,S-coordination of their ligands.

3.4.3. Low-temperature ¹H NMR studies

As mentioned above, at room temperature the ¹H NMR spectra of compounds **1–8** show either one peak or no peak due to the –N(1)H₂ protons. At low temperature, however, two peaks are obtained, due to restricted rotation of the –N(1)H₂ group about the C(1)–N(1) bond. As the temperature is raised these two peaks coalesce at a temperature T_c from which the energy barrier to rotation of the –N(1)H₂ group about C(1)–N(1) can be obtained using the modified form of the Gutowsky–Holm equation [12,27],

$$\Delta G^* = T_c[0.191 - 0.019 \log(\Delta\nu/T_c)] \quad (\text{kJ mol}^{-1}) \quad (1)$$

where ΔG^* is the free energy of activation, T_c the coalescence temperature in K, and $\Delta\nu$ the linewidth in Hz at the half-height of the coalescence peak.

In this study it was possible to determine coalescence temperatures for **7** and **8**, but for **1–6** the complexity of the spectra prevented quantitative analysis. The resulting calculated barrier to rotation of the –N(1)H₂ group about C(1)–N(1) is somewhat higher in **7** than in **8** (Table 7), which is in keeping with the average C(1)–N(1) bond length in the solid state being shorter in **7** than in **8**. In both cases, the barrier is somewhat higher than in thiosemicabazonates of phenylmercury [11,12].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 166259–166261 for compounds **1**, **7** and **8**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK

Table 5
 ^{13}C NMR data (δ , ppm; J , Hz) for diphenylthallium(III) thiosemicarbazonates ^a

Compound	Thiosemicarbazonate moiety		Ligand ring carbons	Ph_2Tl^+ moiety				
	C(1)	C(2)		C_i ($^1J_{13\text{C}-205\text{Tl}}$)	C_o ($^2J_{13\text{C}-205\text{Tl}}$)	C_m ($^3J_{13\text{C}-205\text{Tl}}$)	C_p ($^4J_{13\text{C}-205\text{Tl}}$)	
1	174.8	172.5	34.9, 34.1, 31.6 [C(3,6)], 25.4, 25.2, 24.8 [C(4,5)]	163.6(4390)	137.9(312)	129.8(420)	129.2(75.5)	
2	176.0	145.9	135.1 [C(3)], 130.1 [C(6)], 129.0, 128.8 [C(4,8)], 127.8 [C(5,7)]	165.0(4377)	137.5(324)	130.1(427)	129.1(117)	
4	175.5	145.7	161.9, 161.4 [C(6)], 129.3, 128.8 [C(5,7)], 127.7 [C(3)], 114.5 [C(4,8)], 55.7 [C(9)]	164.6(4287)	137.6(325)	130.1(426)	129.6(80)	
5	174.5	152.6	130.0–126.7 [C(3–8)], 20.0 [C(9)]	^b	^b	^b	^b	
6	176.2	140.3	148.7 [C(3)], 144.2 [C(6)], 116.3 [C(4)], 113.3 [C(5)]	164.0(4528)	137.3(316)	129.8(434)	129.0(84)	
7	181.9	145.5	151.0 [C(3)], 148.9 [C(7)], 138.8 [C(5)], 124.8 [C(4)], 126.5 [C(6)]	164.0(5044)	137.1(315)	129.5(455)	128.5(85)	
8	179.1	148.0	153.1 [C(3)], 148.3 [C(7)], 139.0 [C(5)], 124.4 [C(4)], 123.7, 123.4 [C(6)], 15.9 [C(9)]	164.6(5137)	137.1(312)	129.4(453)	128.2(77)	

^a Compound **3** has poor solubility in CDCl_3 but all the other complexes were soluble.^b Overlapping ligand ring carbons.Table 6
 ^{205}Tl NMR data (δ , ppm) for diphenylthallium(III) thiosemicarbazonates ^a

Compound	Peak I	Peak II	Peak III
1	3741(78.8)	3626(9.5)	3498(11.7)
2	3732(5.0), 3765(7.0)	3627(88.0)	
3^b	3735(12.6)	3612(79.7)	3466(3.5)
4	3766(6.4), 3736(4.9)	3631(88.7)	
5^c	3728(58.2)	3635(39.0)	
6	3759(7.1)	3662(81.7), 3627(11.2)	
7			3461(100)
8			3471(100)

^a Percentage of each peak is given in parentheses.^b Compound **3** has an additional signal at 3833 (4.2%).

Table 7

Calculated barrier to rotation of the $\text{N}(1)\text{H}_2$ group about the $\text{C}(1)-\text{N}(1)$ bonds of complexes **7** and **8** with average $\text{C}(1)-\text{S}$ and $\text{C}(1)-\text{N}(1)$ distances

Compound	T_c (K)	$\Delta\nu$ (Hz)	$\Delta G_{T_c}^\ddagger$ (kJ mol ⁻¹)	$d(\text{C}(1)-\text{S})$ (Å)	$d(\text{C}(1)-\text{N}(1))$ (Å)
7	229	134.6	44.74	1.720(10)	1.337(10)
8	223	139.0	43.46	1.733(8)	1.352(9)

(fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Tables listing detailed crystallographic data, atomic positional parameters and bond lengths and angles are available from the authors on request.

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