

Complexes of 4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazole with monoorganomercury and diorganothallium derivatives. Crystal structure of dimethyl(4-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazolato)thallium(III)

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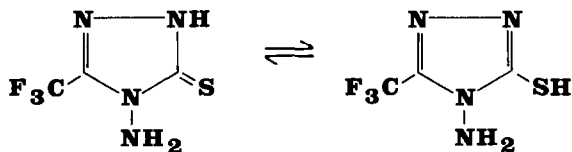
(Received October 2nd, 1987)

Abstract

The compounds R_nML ($M = \text{Hg}$ or Tl , $R = \text{Me}$ or Ph , $n = 1$ or 2 and $L = 4\text{-amino-5-mercapto-3-trifluoromethyl-1,2,4-triazolato}$) have been isolated. The crystal structure of the dimethylthallium(III) compound has been determined. It crystallizes in monoclinic space group $P2_1/c$, with a 11.619(1), b 8.413(1), c 11.698(4) Å, β 108.65(2)° and $Z = 4$. Refinement converged to $R = 0.090$ for 1103 unique observed reflections. The coordination polyhedra of the thallium atom can be described as a very distorted octahedron with a vacant equatorial position directed towards another thallium atom at a distance of 4.14 Å. The structures of the other compounds are discussed in the light of the IR and ^1H NMR data.

Introduction

As part of a programme concerned with comparisons of coordination behaviour of $R_2\text{Tl}^+$ and RHg^+ ($R = \text{Me}$ or Ph) we describe here some features of the compounds isolated from the reaction of these cations with the title triazole (HL):



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For this ligand there is a tautomeric equilibrium between the thiol–thione species. In the solid state both tautomeric forms seem to be present judged from the available spectroscopic information [1], but in solution and in the presence of “soft” cations, it can be expected that the thiol form will be adopted, giving thiolic derivatives. In such derivatives the exocyclic and/or endocyclic nitrogen atoms can form additional coordinative bonds to the metals.

Complexes of HL have been described before [1,2] and their spectroscopic characteristics interpreted in terms of chelation through thiolic and amino groups. There appears, however, not have been any X-ray diffractometric characterisation of these compounds.

Experimental

Materials

The ligand, Me_2TlI , and Ph_2TlBr were prepared by published methods [3]. MeHgCl and PhHgCl were commercial products.

Preparation of compounds

The following general procedure was used. An aqueous solution of the corresponding organometallic hydroxide (obtained by reaction of the organometallic halide with an aqueous suspension of freshly precipitated Ag_2O) was added slowly with stirring to a methanol solution of a ca. equimolar amount of the ligand. The solids which separated were isolated, washed, and dried in vacuo over CaCl_2 . As a typical example, Me_2TlI was obtained by reaction of an aqueous solution of 2.085 g (0.008 mol) of Me_2TlOH with 1.466 (0.0076 mol) of HL in methanol. The pale blue precipitate was recrystallized from methanol to give pale-yellow crystals, which were dried as indicated above.

The elemental analyses for carbon and hydrogen were performed in the case of mercury compounds by Galbraith Lab. Inc., Knoxville, TN, USA and for other species in a Perkin–Elmer 250B apparatus. The metal was determined as before [4], but the methylmercury compound did not give satisfactory results, possibly because of its volatility, but the C and H analysis, together with the integration of the ^1H NMR spectrum of the compound adequately confirmed the stoichiometry proposed (see Table 1).

Table 1
Elemental analyses and some physical properties of the compounds

Compounds	Analysis (Found (calcd.) (%))			Colour	M.p. ($^{\circ}\text{C}$)
	M	C	H		
Me_2TlI	47.9(49.0)	14.5(14.4)	1.9(1.9)	Pale-yellow	190(dec.)
Ph_2TlI	37.7(37.8)	32.9(33.2)	2.1(2.2)	White	130
MeHgI	–	12.1(12.0)	1.3(1.3)	White	127–128
PhHgI	43.6(43.6)	23.3(23.4)	1.6(1.5)	White	154–155

Physical measurements

IR spectra were recorded with Nujol mulls or pressed KBr disks on a Perkin–Elmer 180 spectrometer. ^1H NMR (and ^{13}C NMR for MeHgL) spectra were recorded with a Varian FT-80-A or a Bruker WM 250 spectrometer.

X-Ray data

A crystal of dimensions $0.40 \times 0.33 \times 0.15$ mm was used. Lattice parameters were calculated from the settings of 25 centered reflections with $22^\circ \leq 2\theta \leq 37^\circ$. Intensi-

Table 2

Diffraction data for Me₂TlL

Space group	$P2_1/c$
Formula	$\text{C}_5\text{F}_3\text{H}_9\text{N}_4\text{STl}$
a (Å)	11.619(1)
b (Å)	8.413(1)
c (Å)	11.698(4)
β (deg)	108.65(2)
V (Å ³)	1083.4
Z ($M_r = 417.6$)	4
D_x (Mg m ⁻³)	2.56
μ (mm ⁻¹)	14.5
λ (Mo- K_α graphite monochromator)	0.71073
Measured unique reflections	2645
with $I \geq 3\sigma(I)$	1103
Final R , R_w	0.090, 0.087

Table 3

Final fractional coordinates ($\times 10^3$) and isotropic thermal parameters for Me₂TlL (e.s.d. in parentheses)

	x	y	z	B_{iso} (Å ²)
Tl	72.8(1)	348.9(2)	401.2(1)	3.09(3)
S	118.0(8)	64(1)	292.1(8)	4.5(3)
N(1)	353(2)	137(3)	309(2)	2.8(7)
C(2)	230(3)	123(4)	233(3)	3.0(10)
N(3)	223(3)	168(4)	121(3)	5.0(10)
N(4)	340(3)	202(3)	123(2)	3.3(8)
C(5)	411(3)	185(3)	233(3)	2.7(9)
C(6)	545(3)	219(5)	274(3)	4.0(10)
N(7)	405(3)	110(3)	432(2)	4.0(9)
C(8)	-65(3)	239(4)	458(3)	3.8(6)
C(9)	204(3)	487(4)	355(3)	4.0(10)
F(1)	577(2)	327(2)	353(2)	5.9(8)
F(2)	578(2)	262(3)	181(2)	7.0(10)
F(3)	607(2)	85(3)	319(2)	5.1(7)
Hydrogen atoms found from the difference map				
H(71)	401.1	191.6	505.6	4.0
H(72)	427.4	-8.1	475.5	4.0
H(81)	856.0	184.1	447.3	4.0
H(91)	236.9	579.9	433.8	4.0
H(92)	283.7	414.8	367.2	4.0
H(93)	170.4	543.3	278.0	4.0

ties of 6056 reflections with $2\theta < 50^\circ$ were measured in the $\omega/2\theta$ mode on a CAD-4 diffractometer. A constant speed of $10^\circ \text{ min}^{-1}$ and a variable scan width of $(0.80 + 0.35 \tan \theta)^\circ$ were used. Two standard reflections were measured every 30 min with variation less than 1%. The data were corrected for Lorentz and polarization effects but not for absorption or extinction since there were no easily identifiable faces on the crystal used for data collection.

The Patterson function was used to locate the Tl atom, and electron density maps then used to locate all the other atoms except for two H atoms attached to the C(8) atom. Anisotropic refinement was carried out for all atoms except hydrogens by full-matrix least squares using SHELX-76 [5], to give $R_w = 0.087$, $w = (\sigma^2 + (kF_0)^2)^{-1}$, σ is the standard error in F_0 derived from counting statistics and $k = 0.018635$. It was necessary to use isotropic thermal parameters for the C(8) atom.

Atomic scattering factors corrected for anomalous dispersion were taken from ref. 6. The mean and maximum value of shift/error was 0.02 and 0.04, respectively. A difference synthesis showed two peaks at circa 1 Å distance from the Tl atom, with an electron density of $6.8 \text{ e}\text{\AA}^{-3}$, that may be attributed to series termination errors and to the neglect of absorption correction. No other peak had an integrated electron density greater than $1.7 \text{ e}\text{\AA}^{-3}$. The relevant diffraction data and the final atomic coordinates are listed in Tables 2 and 3, respectively.

Results and discussion

X-Ray structure

An ORTEP [7] view of the crystal packing of Me_2Tl with atomic labelling is shown in Fig. 1. Table 4 list the crystallographically determined bond distances and angles.

The thallium atom is coordinated by two carbon atoms, one sulphur atom from a ligand molecule, and a N(1) atom from another such molecule. The lengths of these bonds are quite normal and similar to those found in other compounds with heterocyclic thiols [8]. The coordination polyhedron of thallium atom is made up to five by a weak interaction involving a bridging sulphur atom from a third molecule of the ligand, the $\text{Tl} \cdots \text{S}$ distance being rather large but below the sum of the Van der Waals radii [9]. In addition to these coordinated ligands, the thallium atom has another thallium atom at 4.14 Å at a point generated by the inversion center in the A face of the unit cell (Fig. 1). This distance, which is more than twice the Van der Waals radius of thallium (3.92 Å, ref. 9) and shorter than that observed in the phenylalanine derivative [10], seems to indicate the absence of any significant metal-metal interaction, and so the coordination polyhedron of the thallium can be described as a very distorted octahedron with a vacant equatorial position.

The Me_2Tl unit is nearly linear (the C(8)-Tl-C(9) angle is 173°) as is usually the case in dimethylthallium compounds (see ref. 8, and references therein). The atoms in the plane S-C(5)-N(1)-N(2)-C(3)-N(4)-N(7) are coplanar within the standard deviation. In contrast to the situation in (DL-triptophanato)dimethylthallium(III) [11], the amino group is not coordinated to the metal. The C(5)-S distance is the same found in $\text{Me}_2\text{Tl}(\text{HTu})$ [8] and indicates that this bond retains some double-bonded character.

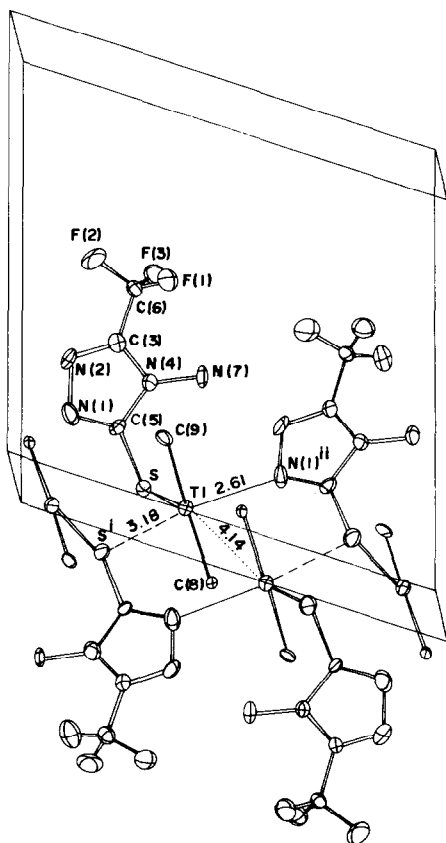


Fig. 1. The environment of the thallium atom in Me_2TIL and the numbering scheme used.

The crystal packing consists of strips of dimerized molecules along the c direction interconnected by $\text{N}(7)\text{--N}(7)$ hydrogen bond interactions (see Fig. 2). Within these strips the molecules are connected by the $\text{Tl}\text{--N}(1)$ and $\text{Tl}\dots\text{S}$ interactions and through hydrogen bonds between the NH_2 group and the $\text{N}(2)$ atom of neighbouring molecules (Fig. 2). The $\text{N}(7)\text{--N}(7)^{\text{iii}}$ and $\text{N}(2)^{\text{ii}}\text{--N}(7)$ intermolecular distance (respectively 2.93(4) and 3.02(4) Å) are within the usual range for this bond [12].

IR spectra. For the assignment of the ligand vibrations, the criterion used previously [1,2a], based on the thioamide I, II, III and IV bands, was used. In the complexes prepared in this work these bands (Table 5) lie close to the positions previously observed [1,2a]. This, and the disappearance upon coordination of the weak band present at 2580 cm^{-1} in the free ligand that can be ascribed to $\nu(\text{S}\text{--H})$, indicate that the coordination is through the thiolic sulphur atom after deprotonation of the ligand.

The $\nu(\text{NH}_2)$ mode in the free ligand undergoes a slight shift towards lower wavenumbers in the complexes, suggesting the presence of hydrogen bonds similar to those detected in Me_2TIL .

Table 4

Interatomic distances (Å) and angles (°)

Tl–C(8)	2.11(3)	C(8)–Tl–C(9)	173(2)
–C(9)	2.13(3)	C(8)–Tl–S	92(1)
–S	2.85(1)	C(8)–Tl–S ⁱ	93(1)
...S ⁱ	3.18(3)	C(8)–Tl–N(1) ⁱⁱ	90(1)
...N(1) ⁱⁱ	2.61(2)	C(9)–Tl–S	95(1)
...Tl ⁱⁱⁱ	4.14(1)	C(9)–Tl–S ⁱ	84(1)
		C(9)–Tl–N(1) ⁱⁱ	88(1)
S–C(5)	1.73(3)	S–Tl–S ⁱ	110(1)
N(1)–C(5)	1.34(5)	S ⁱ –Tl–N(1) ⁱⁱ	146(1)
N(4)–C(5)	1.41(4)	S–Tl–N(1) ⁱⁱ	104(1)
N(4)–C(3)	1.34(4)	C(5)–S–Tl	102(1)
N(4)–N(7)	1.39(3)	S–C(5)–N(4)	120(2)
N(1)–N(2)	1.37(4)	S–C(5)–N(1)	131(3)
N(2)–C(3)	1.30(4)	N(4)–C(5)–N(1)	109(3)
C(3)–C(6)	1.50(4)	C(5)–N(4)–N(7)	131(3)
C(6)–F(1)	1.27(4)	C(3)–N(4)–N(7)	126(3)
C(6)–F(2)	1.32(4)	C(3)–N(4)–C(5)	103(3)
C(6)–F(3)	1.35(4)	N(2)–C(3)–N(4)	113(3)
N(7)–N(2) ⁱⁱ	3.02(4)	C(5)–N(1)–N(2)	107(3)
N(7)–N(7) ⁱⁱⁱ	2.93(4)	N(1)–N(2)–C(3)	108(3)
		N(4)–C(3)–C(6)	123(3)
Symmetry code		N(2)–C(3)–C(6)	124(3)
(i) $-x, 1/2 + y, 1/2 - z$		C(3)–C(6)–F(1)	114(3)
(ii) $x, 1/2 - y, 1/2 + z$		C(3)–C(6)–F(2)	110(3)
(iii) $1 - x, -y, 1 - z$		C(3)–C(6)–F(3)	110(3)
		F(1)–C(6)–F(2)	108(3)
		F(1)–C(6)–F(3)	109(3)
		F(2)–C(6)–F(3)	106(3)
		N(7)–H(71)...N(7) ⁱⁱⁱ	130(2)
		N(7)–H(72)...N(2) ⁱⁱ	160(1)

The band from $\delta_{\text{sym}}(\text{CH}_3)$ in MeHgL must be located in the region of the C–F stretching modes (1200–1140 cm^{-1} in the ligand and complexes), and so it cannot be assigned. The $\nu(\text{Hg}–\text{C})$ bands appears at 545 cm^{-1} , within the typical range of coordination via thiolic sulphur atoms [13]. In Me₂TiL, $\rho(\text{CH}_3)$ appears at 800 cm^{-1} and $\nu_{\text{asym}}(\text{C}–\text{Tl}–\text{C})$ at 550 cm^{-1} , both as medium bands. In PhHgL and Ph₂TiL, the t-mode (the “X-sensitive” band in Whiffen’s notation [14], the band most affected by coordination to the metal atom), normally situated close to 250 cm^{-1} [14,15,16] is obscured by ligand bands. All the complexes show several bands that in the 400–300 cm^{-1} range can be attributed to the M–S stretching mode, although probably they are not pure bands.

¹H NMR spectra. Association of Me₂TiL in the solid state accounts for the low solubility of the compound in organic solvents with low donor abilities. Similar behaviour was observed for the other compounds synthesized. However all the complexes are sufficiently soluble in DMSO-*d*₆ for determination of the ¹H NMR spectra (and also the ¹³C NMR spectrum in the case MeHgL). The spectroscopic parameters of the organometallic part of the compounds (Table 6) give some indication of the coordination situation in the solutions. The coupling $^2J(^{203,205}\text{Tl}–^1\text{H})$ in Me₂TiL has the usual value found for other heterocyclic thiol

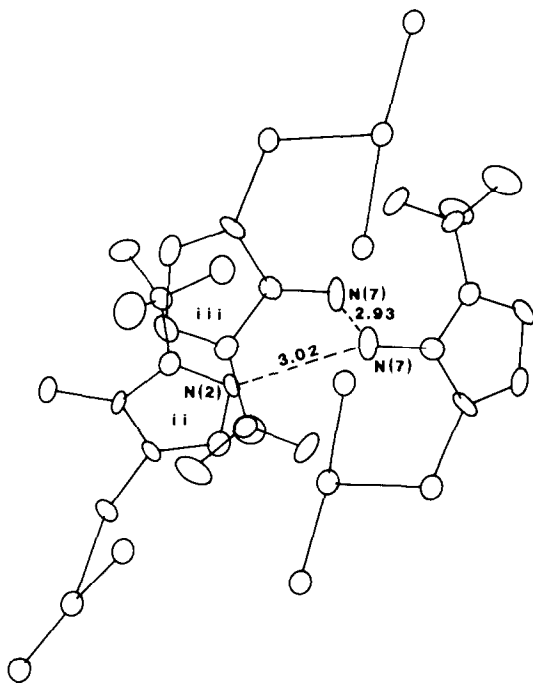


Fig. 2. Hydrogen bond interactions in Me_2TIL .

Table 5

$\nu(\text{NH}_2)$ and thioamide bands for the ligand and complexes

Compound	$\nu(\text{NH}_2)$	I	II	III	IV
HL	3320s,3300s,3200s,b	1580m	1250s	1090m	770m
MeHgL	3320s,3260m,3180s	1535s	1260s	1055m	720m
Me_2TIL	3340s,3200s,b	1535s	1255s	1040m	730m
PhHgL	3270s,3140m,3100m	1525s	1270s	1055w	745m
Ph_2TIL	3340,3240m	1540s	1250s	1060m	735m

Table 6

Relevant ^1H NMR spectral data for the organometallic parts of the complexes (δ in ppm from TMS; J in Hz; solvent $\text{DMSO}-d_6$)

Compounds	$\delta(\text{MR}_n)$	$^nJ(\text{M}-\text{H})$
MeHgL	0.77	192.7
Me_2TIL	0.84	420
PhHgL	7.45 (H_o)	–
	7.35 (H_m)	–
	7.27 (H_p)	–
Ph_2TIL	7.81 (H_o)	454
	7.44 (H_m)	138
	7.27 (H_p)	52

derivatives [17] for which additional nitrogen-coordination cannot be ruled out. The value of $^2J(^{199}\text{Hg}-^1\text{H})$ in MeHgL indicates that there is only a thiolic bond and excludes simultaneous or alternative nitrogen coordination. The shift of the ^{13}C NMR signal of the methyl group (8.98 ppm) confirms this view [18].

Supplementary material. Tables of anisotropical thermal parameters and of observed and calculated structure factors are available from the authors.

Acknowledgements

We thank Dr. Agustín Sánchez for helpful discussions. This work was supported by the CAICYT and the CSIC (Spain), and by FAPESP, CNPq and FINEP (Brazil).

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