SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF DIMETHYL (DIETHYLMONOTHIOCARBAMATO)THALLIUM(III), [$TlMe_2\{S(O)CNEt_2\}$]

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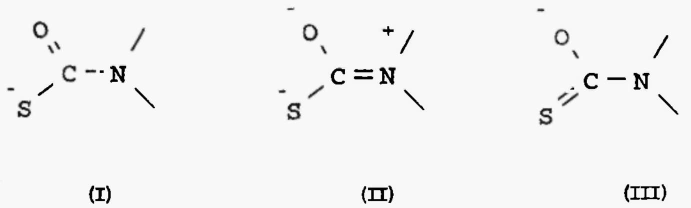
Abstract

Dimethyl(diethylmonothiocarbamato)thallium(III), [$TlMe_2\{S(O)CNEt_2\}$] was synthesized by reacting $TlMe_2(NO_3)$ and [Et_2NH_2][$S(O)CNEt_2$] in ethanol. The compound crystallized in the monoclinic space group $P2_1/n$ (No. 14) with a= 7.3379(4), b= 8.030(1), c= 19.032(3) Å and β= 100.611(8)°, V= 1102.2(2) Å^3 and Z= 4. The structure consists of [$TlMe_2\{S(O)CNEt_2\}$] units in which the thallium atom is coordinated to the two methyl carbons and to the S and O atoms of the bidentate monothiocarbamato (Tl-S = 2.766(3), Tl-O = 2.684(7) Å). These units are connected by additional Tl-O bonds (Tl-O^{ii} = 2.690(7) Å) and weak Tl-S interactions (Tl-S^{i}= 3.315(3) Å), giving rise to a supramolecular polymeric ribbon along the b axis with practically symmetrical Tl-O-Tl bridges. The IR and ^1H and ^{13}C NMR spectra of the compound are also discussed.

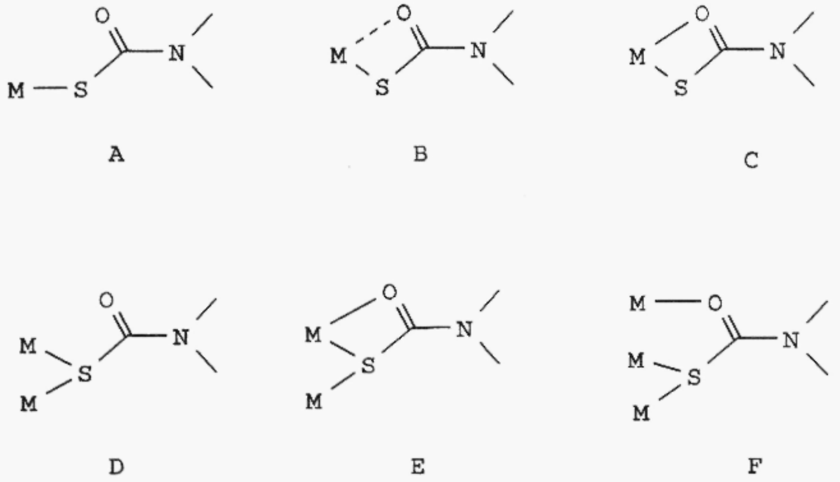
Introduction

The coordination chemistry of monothiocarbamates (mtc´s) [1] has been explored much less thoroughly than that of dithiocarbamates (dtc´s) even though it seems probable that mtc complexes must be chemically and structurally different from dtc complexes [2] because of their greater mercaptide character. This mercaptide nature is attributable to a predominant contribution of the resonance forms labelled I and II in Scheme I [3]; in particular, the nonequivalence of the NMR signals from equal R groups bound to the nitrogen atom suggests a major contribution by resonant form II.



Scheme I

Six different coordination modes have been observed in mtc complexes (Scheme II) [2]



Scheme II

(most of which feature C-O bond lenghts suggesting some double bond character), but only a few organometallic mtc´s have been reported, they include organotin(IV) [2a] and organotellurium(IV) [4] derivatives. This prompted us to react $[Et_2NH_2][S(O)CNEt_2]$ with the dimethylthallium(III) cation, and to analyze the structural and spectroscopic properties of the new mtc thus obtained.

Materials and Methods

Diethylamine, thallium(I) iodide (Merck) and carbonyl sulfide (Aldrich) were used as received. Diethylammonium diethylmonothiocarbamate, $[Et_2NH_2][S(O)CNEt_2]$, was synthesized as per McCormick *et al.* [1]. Dimethylthallium(III) nitrate was obtained [5] by reaction of nitric acid with a dimethylthallium(II) hydroxide prepared by treating $TlMe_2I$ with a freshly prepared suspension of silver oxide in water [6].

Elemental analysis was performed in a Carlo Erba 1108 analyzer. IR spectrum was recorded in KBr disc with a Perkin Elmer 1330 spectrometer. ^1H (250.13 MHz) and $^{13}C\{^1H\}$ (62.86 MHz) NMR spectra were obtained on a Bruker WM-250 spectrometer and referred to TMS using the solvent ($CDCl_3$) signal (^1H, 7.27 ppm; ^{13}C, 77.00 ppm).

Synthesis of dimethyl(diethylmonothiocarbamato)thallium(III), $[TlMe_2\{S(O)CNEt_2\}]$.

A solution of $[Et_2NH_2][S(O)CNEt_2]$ (0.17 g, 0.82 mmol) in ethanol (15 cm^3) was added to $TlMe_2(NO_3)$ (0.24 g, 0.81 mmol) dissolved in the same solvent (10 cm^3) at 0°C. The resulting mixture was filtered and the filtrate was vacuum concentrated and stored at 0°C. After 3 days, the colourless crystals formed were filtered out and air dried. M.p.: 110°C (*Anal.* Found: C 22.3, H 4.3, N 4.1; $C_7H_{16}NOSTl$ requires C 22.9, H 4.4, N 3.8%).

Crystal structure determination of [TlMe$_2${S(O)CNEt$_2$}]

A colourless prismatic crystal of approximately 0.12x0.25x0.30 mm in size was used in X-ray analysis.

Crystal data. $C_7H_{16}NOSTl$, M = 366.65, monoclinic, space group $P2_1/n$ (No. 14), a = 7.3379(4), b = 8.030(1), c = 19.032(3) Å and β = 100.611(8)°, V = 1102.2(2) Å^3, Z = 4, D_{calc} = 2.209 g cm^{-3}, F(000) = 680 and μ(Mo-K$_\alpha$) = 149.23 cm^{-1}.

Data for structure determination were obtained at room temperature on a CAD-4 Enraf-Nonius automatic diffractometer using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.70930 Å). The $\omega/2\theta$ scan technique was used. 2503 reflections were collected in the θ range 3-26°. Of 2141 independent reflections (R_{int} = 0.027), 1666 with $I > 3\sigma(I)$ were used for refinement. An empirical absorption correction was applied [7]. The secondary extinction coefficient refined to 1.760×10^{7}.

The structure was solved using direct methods and subsequent Fourier difference maps. All non-H atoms were refined with anisotropic displacement parameters. The position of all H atoms were calculated geometrically (C-H = 0.95 Å) and included in structure factor calculation with B_{iso} = 4.0 Å^2 fixed, but not refined. Final R and R_w values were 0.031 and 0.037, respectively. The maximum height in the final ΔF map was 1.11 e Å^{-3} around the Tl atom. Most calculations were performed on a DEC MicroVAXII computer with the programs SHELXS86 [8], VAXSDP [9] and SCHAKAL [10].

Table I. Final fractional coordinates and U_{eq} values in [TlMe$_2${S(O)CNEt$_2$}].

Atom	x	y	z	U_{eq} (Å^2)^a
Tl	0.16134(5)	0.97435(5)	0.21787(2)	0.0346(2)
S(1)	0.3404(4)	0.8558(4)	0.3490(2)	0.042(1)
O(1)	0.419(1)	1.1500(8)	0.3059(4)	0.043(4)
N(1)	0.620(1)	1.059(1)	0.4031(4)	0.036(4)
C(1)	0.369(1)	0.944(2)	0.1529(6)	0.052(6)
C(2)	-0.093(2)	1.028(2)	0.2520(7)	0.069(7)
C(3)	0.468(1)	1.040(1)	0.3506(5)	0.030(4)
C(11)	0.687(2)	0.936(1)	0.4570(6)	0.047(6)
C(12)	0.835(2)	0.827(2)	0.4349(7)	0.058(7)
C(21)	0.729(1)	1.214(1)	0.4047(6)	0.046(6)
C(22)	0.673(2)	1.345(2)	0.4548(7)	0.07(1)

^{a} U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Structure of dimethyl(diethylmonothiocarbamato)thallium(III), [$TlMe_2\{S(O)CNEt_2\}$].

Tables I and II list atomic coordinates and selected bond distances and angles in the new compound.

Table II. Main bond distances (Å) and angles (°) in [$TlMe_2\{S(O)CNEt_2\}$].

Tl-C(1)	2.14(1)	Tl-S(1)′	3.315(3)
Tl-C(2)	2.13(1)	S(1)-C(3)	1.75(1)
Tl-O(1)	2.684(7)	O(1)-C(3)	1.24(1)
Tl-S(1)	2.766(3)	N(1)-C(3)	1.36(1)
Tl-O(1)"	2.690(7)		
C(1)-Tl-C(2)	162.5(4)	S(1)-Tl-C(1)	102.2(3)
S(1)-Tl-O(1)	57.0(2)	S(1)-Tl-C(2)	95.3(3)
O(1)-Tl-O(1)"	132.1(3)	S(1)′-Tl-O(1)	78.9(2)
O(1)-Tl-C(1)	85.8(3)	S(1)′-Tl-O(1)"	146.6(2)
O(1)-Tl-C(2)	104.9(4)	S(1)′-Tl-C(1)	80.5(3)
O(1)"-Tl-C(1)	87.2(4)	S(1)′-Tl-C(2)	89.3(4)
O(1)"-Tl-C(2)	94.2(4)	S(1)-C(3)-O(1)	120.3(7)
S(1)-Tl-S(1)′	129.18(7)	S(1)-C(3)-N(1)	118.1(7)
S(1)-Tl-O(1)"	82.6(2)	O(1)-C(3)-N(1)	121.7(9)

[a] Symmetry code: ′ = ½-x, ½+y, ½-z; " = ½-x, -½+y, ½-z.

Fig. 1 shows that the thallium atom is coordinated to S(1) and O(1), forming a four-membered chelate ring, and to two methyl C atoms; the C-Tl-C moiety is characterized by bond distances and angles (Table II) similar to those found in other complexes of dimethylthallium(III) with anionic ligands [11]. The metal atom is also bound to the oxygen atom of a neighbouring

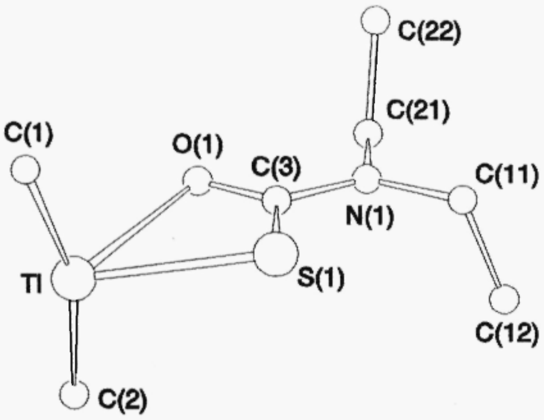


Figure 1. SCHAKAL plot of [$TlMe_2\{S(O)CNEt_2\}$], showing the atomic numbering scheme used.

molecule (Tl-O(1)") (Fig. 2), giving rise to a supramolecular polymeric ribbon with practically symmetrical Tl-O-Tl bridges (Tl-O(1) = 2.684(7), Tl-O(1)" = 2.690(7) Å) that have not previously been observed in diorganothallium(III) complexes with S,O-coordinated ligands [1, 12]. This polymer structure is reinforced by weak Tl...S interactions (Tl-S(1)′ = 3.315(3) Å, sum of Van der Waals radii 3.75 Å [13]). If all these strong and weak interactions are included, the thallium atom can be described as possesing a distorted octahedral coordination polyhedron. The main distorted angles are C(1)-Tl-C(2) (162.5(4)°) and S(1)-Tl-O(1) (57.0(2)°), the value of the latter being imposed by the bite of the ligand.

The Tl-S(1) distance is shorter than that found in diorganothallium(III) complexes with S,S′-ligands, such as dithiophosphinate [14-16], phosphinodithioformate [17], xanthate [18] and tetraphenyldithioiminodiphosphinate [19]; and is slightly longer than the mean Tl-S distance in diorganothallium (III) dithiocarbamates [20, 21]. The Tl-O(1) distance is longer than the intra-unit Tl-O distances found in other thallium (III) complexes with anionic O,X ligands, such as acetate, tropolonate, acetylacetonate (X= O) [22] and 1-oxidopyridinium-2-thiolate (X= S) [11], but in all these complexes except the acetate there is also a longer inter-unit Tl-O distance, and the Tl-O-Tl bridges in these compounds are in fact more asymmetrical than in [$TlMe_2\{S(O)CNEt_2\}$].

As in [$TlMe_2\{S(O)PPh_2\}$] and [$TlMe_2(S_2PPh_2)$] [12, 14], the supramolecular arrangement in [$TlMe_2\{S(O)CNEt_2\}$] is more regular than in [$TlMe_2(S_2CNPr_2)$] [21]. It is similar to that observed in dimethylthallium(III) acetate [22], although in the acetate the chelate rings are practically co-planar. In the mtc complex the weak inter-unit Tl...S interactions possibly hinder ring coplanarity due to the habitual preference of the sulphur atom for pyramidal coordination [12, 20].

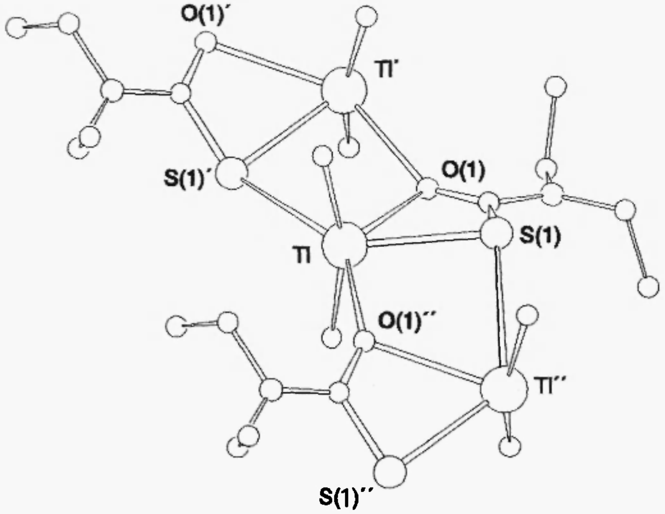
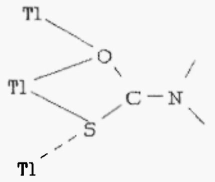


Figure 2. SCHAKAL plot showing polymeric structure in [$TlMe_2\{S(O)CNEt_2\}$].

The bond distances in the planar monothiocarbamato group (SCON) differ somewhat from those found in dimethyltellurium(IV) diethylmonothiocarbamates [4]. In the tellurium compounds, the C-S distance is longer and the C-O and C-N distances shorter than in the thallium compound. Note that in $Me_2Te(IV)$ monothiocarbamates the ligand is basically monodentate, with only a weak secondary Te...O interaction (coordination mode B in Scheme II), and π electron delocalization extends to the C-N bond; in comparison, in [$TlMe_2\{S(O)CNEt_2\}$] the π electrons are more localized on the SCO moiety and the C-S bond acquires more double bond character at the expense of the C-O and C-N bonds. The coordination mode of the ligand in [$TlMe_2\{S(O)CNEt_2\}$] is new for monothiocarbamates and can be roughly described as in Scheme III.



Scheme III

IR spectrum

A strong, broad band in the spectrum of the complex at 1500 cm^{-1} is assigned to $\nu(C\underline{\cdot\cdot}O)$ + $\nu(C\underline{\cdot\cdot}N)$ [23], which places this mode outside the range found in S-monodentate complexes [3]. The assignation of $\nu(C\underline{\cdot\cdot}S)$ to a band at 940 cm^{-1} is in keeping with the structural results. As regards the organometallic fragment, a strong band at 780 cm^{-1} is attributed to $\rho(CH_3)$, and medium and weak bands at 540 and 480 cm^{-1} to ν_{asym}(C-Tl-C) and ν_{sym}(C-Tl-C) respectively.

NMR spectra.

^1H and $^{13}C\{^1H\}$ NMR data for the new compound and the diethylammonium salt of the ligand in $CDCl_3$ are listed in Table III. In [Et_2NH_2][$S(O)CNEt_2$] spectrum two groups of signals are

Table III. Significant NMR data of the diethylammonium salt of the ligand and dimethylthallium complex^a.

			[Et_2NH_2][$S(O)CNEt_2$]	[$TlMe_2\{S(O)CNEt_2\}$]
^1H data	$\delta[NH_2]^c$		8.16 s, br (2)	---
	$\delta[C(11)H_2]$	$\}^b$	3.83 vbr (2)	3.53 q (2)
	$\delta[C(21)H_2]$		3.37 vbr (2)	3.31 q (2)
	$\delta[CH_2]^c$		2.93 q (4)	---
	$\delta[CH_3]^c$		1.31 t (6)	---
	$\delta[C(12)H_3]$	$\}^b$	1.11 vbr (3)	1.23 t (3)
	$\delta[C(22)H_3]$		1.09 vbr (3)	1.12 t (3)
	$\delta[TlMe_2]$		---	1.32 d (6)
	$^2J(^1H\text{-}^{205}Tl)$		---	354
^{13}C	$\delta[C(3)]$		184.1	183.4
	$\delta[C(11)]$	$\}$	45.4	49.9
	$\delta[C(21)]$		40.1	41.9
	$\delta[CH_2]^c$		41.6	---
	$\delta[CH_3]^c$		11.2	---
	$\delta[C(12)]$	$\}$	13.2	13.2
	$\delta[C(22)]$			
	$\delta[TlMe_2]$		---	23.43 d
	$^1J(^{13}C\text{-}^{205}Tl)$		---	2319

[a] $CDCl_3$ as solvent, δ in ppm, J in Hz. In parentheses relative number of protons. s= singlet; d= doublet; t= triplet; q= quartet; br= broad; vbr= very broad.
[b] For numbering scheme see Fig 1. [c] From [Et_2NH_2]$^+$.

distinguishable, one attributable to the diethylammonium cation and the other to the monothiocarbamate anion. The cation group contains the -NH_2 signal at 8.16 ppm and two other well-resolved multiplets attributable to the ethyl group. The anion group consists of two sets of poorly resolved signals (attributable to two different Et groups); this situation differs from that found in the spectra of dithiocarbamates [21, 24] and suggests restriction of rotation around the C-N bond. ^{13}C spectrum corroborates the foregoing: the ethyl groups of the cation appear as two signals, one for each kind of carbon, whereas the anionic part of the spectrum features two peaks for the methylene carbons (although there is only one for the methyl carbons); the peak at lowest field belongs to C(3).

As can be expected, the ^1H spectrum of the complex shows none of the signals attributed to $[Et_2NH_2]^+$. The fact that the monothiocarbamate peaks still form two groups would appear to indicate that rotation around the C-N bond keeps restricted despite the reduction in π electron delocalization indicated by the solid state structure. In consonance with this, the ^{13}C spectrum again shows two signals for the methylene carbons.

The position of the organometallic proton signals in the ^1H spectrum of the complex is similar to that found in $[TlMe_2(S_2CNPr_2)]$ (1.33 ppm [25]), and the ^2J value is of the same order as in the latter compound (355 Hz [25]), or in other dtc ($[TlMe_2(S_2CNMe_2)]$ [26] and $[TlMe_2(S_2CNEt_2)]$ [26]). These parameters thus appear to be insensitive to the nature of the donor atoms in this type of ligands. The ^{13}C signals appear to be more sensitive, showing less shielding and ^1J coupling in the mtc than in $[TlMe_2(S_2CNPr_2)]$ [21].

Acknowledgements.
We thank the Xunta de Galicia, Spain, for financial support.

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Received: January 19, 1996 - Accepted: January 29, 1996 - Accepted in revised camera-ready form: February 14, 1996