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Dithiocarbamates of dimethylthallium(III). Crystal structure of dimethyl(di-n-propyldithiocarbamato)thallium(III)

José S. Casas, María V. Castaño*, Celestino Freire, Agustín Sánchez and José Sordo
Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15706 Santiago de Compostela (Galicia) (Spain)

Eduardo E. Castellano* and Julio Zukerman-Schpector
Instituto de Física e Química de Sao Carlos, Universidade de Sao Paulo, Caixa Postal 369-CEP, 13560 Sao Carlos, SP (Brazil)

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Abstract

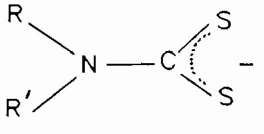
Six solid compounds of composition [$TlMe_2(dtc)$] (where dtc is a dithiocarbamate anion) have been obtained. [$TlMe_2(S_2CN^nPr_2)$] crystallizes in the space group $C2$ with $a = 19.672(2)$, $b = 8.5698(5)$, $c = 9.194(2)$ Å, $\beta = 116.02(1)°$ and $Z = 4$. The thallium atom is coordinated to the two sulfur atoms of a slightly anisobidentate dithiocarbamate ligand and to the two methyl groups, which form a highly distorted tetrahedral environment. In the crystal lattice these units are linked by additional weak Tl···S interactions. The main coordination characteristics of this compound seem to be common to the other complexes prepared, both in the solid state and in solution in $CDCl_3$ or DMSO-d_6, to judge by their spectral (IR and NMR) properties.

Key words: Crystal structures; Dithiocarbamate complexes; Thallium complexes

Introduction

The crystal structures of a number of dimethylthallium derivatives of 1,1′-dithioacid donors, including ethylxanthate [1], diphenylphosphinodithioformate [2] and diphenyldithiophosphinate [3], have been reported. However, it seems that in spite of the versatile coordination behaviour of dithiocarbamates, no structural study of any dimethylthallium dithiocarbamate has been carried out. An investigation of the crystal structure of diphenyl(diethyldithiocarbamato)thallium(III) [4] was not accompanied by a parallel study of the corresponding dimethylthallium complex, which is surprising in view of the interest of the possible structural consequences of replacing the phenyl groups by methyls.

In this paper we describe the synthesis and spectroscopic properties of the following dimethylthallium(III) mono- and dialkyldithiocarbamates, [$TlMe_2L^n$]:



L^n	R	R′
L^1	$-CH_2CH_2CH_3$	$-CH_2CH_2CH_3$
L^2	$-CH_2CH(CH_3)_2$	$-CH_2CH(CH_3)_2$
L^3	$-(CH_2)_3CH_3$	$-(CH_2)_3CH_3$
L^4	$-CH_3$	$-CH_2-CH_2OH$
L^5	$-H$	$-CH_2CH_3$
L^6	$-H$	$-(CH_2)_3CH_3$

We also report the crystal structure of dimethyl(di-n-propyldithiocarbamato)thallium(III). None of these compounds seems to have been prepared before, although Bonati *et al.* isolated dimethylthallium(III) dithiocarbamates [$TlMe_2(S_2CNR_2)$], where R = Me, Et or Ph [5].

Experimental

Materials and instrumentation

Dimethylthallium iodide was obtained by the method of Gilman and Jones [6]. Dimethylthallium hydroxide was prepared by stirring $TlMe_2I$ with excess freshly precipitated silver oxide for 48 h in deionized water and then removing the AgI by filtration. The sodium salts of the ligands were a gift of Professor Mark M. Jones [7]. Elemental analyses were carried out on a Perkin-Elmer 240 B microanalyzer. Conductivity was

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*Authors to whom correspondence should be addressed.

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TABLE 1. Analytical and physical data for the complexes

Compound	C (%)	H (%)	N (%)	M.p (°C)	Colour	Λ^b (S cm^2 mol^{-1})
[$TlMe_2L^1$]	26.5(26.3)^a	3.5(3.4)	5.4(4.9)	123	white	1.9
[$TlMe_2L^2$]	29.6(30.1)	3.4(3.2)	5.8(5.5)	75–76	light yellow	1.2
[$TlMe_2L^3$]	28.9(30.1)	3.5(3.2)	5.8(5.5)	62	yellow	1.5
[$TlMe_2L^4$]	19.8(18.7)	4.1(3.6)	3.9(3.7)	dec	brown	3.6
[$TlMe_2L^5$]	16.8(16.9)	3.8(3.9)	3.5(4.0)	113	brown	6.8
[$TlMe_2L^6$]	21.2(21.8)	3.3(3.7)	4.3(4.2)	92	brown	8.7

[a] Theoretical values in parentheses. [b] Molar conductivity for 10^{-3} M solutions in acetonitrile

TABLE 2. Crystal data

Formula	$C_9H_{20}NS_2Tl$
Molecular weight	410.76
Space group	$C2$
a (Å)	19.672(2)
b (Å)	8.5698(5)
c (Å)	9.194(2)
β (°)	116.02(1)
V (Å^3)	1392.8(7)
Z	4
D_{calc} (g cm^{-3})	1.959
Sample dimensions (mm)	0.18 × 0.15 × 0.10
Radiation (Å)	λ (Mo Kα) = 0.71073
T (K)	293
Linear absorption coefficient, μ (cm^{-1})	119.71
Scan technique	$\omega/2\theta$
Correction factors max., min	2.14, 0.52
θ Range for data collection (°)	0–30
$F(000)$	776
No. reflections measured	1865
No. unique reflections	1774
R_{int} (after absorption correction)	0.018
No reflections above $3\sigma(I)$	1004
Minimized function	$\Sigma w(\|F_o\|-\|F_c\|)^2$
Weighting scheme	$\sigma^2(F_o)+0.0008\|F_o\|^2]^{-1}$
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0539
$R_w=[\Sigma w(\|F_o\|-\|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.0558
$S=[\Sigma w(\|F_o\|-\|F_c\|)^2/(M-N)]^{1/2}$	1.55
h_{min}, h_{max}, k_{min}, k_{max}; l_{min}, l_{max}	−27, 24, 0, 12; 0, 12
Residual ρ max., min (e Å^{-3})	1.71, −2.34

measured in acetonitrile with a WTW LF3 conductimeter. IR spectra (4000–180 cm^{-1}) were recorded in KBr disks on a Perkin-Elmer 180 spectrometer. ^{1}H and ^{13}C NMR spectra in DMSO-d$_6$ and $CDCl_3$ solution were recorded at room temperature on a Bruker WM-250 spectrometer at 250.13 and 62.83 MHz, respectively, and CP MAS ^{13}C spectroscopy was performed on a Bruker MSL-400 apparatus at 100.63 MHz with a sample packed in a 7 mm ZrO_2 rotor spinning at 4.0 kHz (recycle time 10.0 s, acquisition time 41 ms, contact time 1.0 ms).

Syntheses of complexes

To a stirred aqueous solution of $TlMe_2OH$ was slowly added an aqueous solution of the corresponding ligand as sodium salt until a metal:ligand mole ratio of about 1:1 was reached. In each case a precipitate was formed which was filtered off, washed with water and dried under reduced pressure. Analytical and physical data for the complexes are shown in Table 1.

Determination of the structure of [$TlMe_2L^1$]

A transparent crystal of [$TlMe_2L^1$] grown by slow evaporation of a $CHCl_3$ solution was used for intensity data collection on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo Kα radiation. Crystal and refinement data are listed in Table 2. The structure was solved using the heavy atom Patterson method and difference Fourier techniques. Though a substantial part of the electron density was consistent with space group *C2/m*, with all atoms except those of the propyl radicals lying in the mirror plane, refining in this space group showed that the propyl groups were not mirror images. Refinement was therefore carried out in space group *C*2. Some correlation coefficients derived from the full normal equation matrix were pathologically large, giving rise to oscillations in the convergence. In the final cycles of refinement only the Tl and S atoms were treated anisotropically (anisotropic temperature factors of light atoms were ill-behaved, probably due to the quasisymmetry of the structure). H atoms were not included in the model. Data were corrected for Lp and absorption [8]. Scattering factors for non-H atoms were taken from Cromer and Mann [9] with corrections for anomalous dispersion taken from Cromer and Liberman [10]. Programs used: SHELX76 [11] and ORTEP [12]. Most of the calculations were performed on a VAX 6420 computer.

Results and discussion

Structure of [$TlMe_2L^1$]

The numbering scheme is shown in Fig. 1; atomic positions, and bond lengths and angles are listed in Tables 3 and 4, respectively. The thallium atom is coordinated to the two sulfur atoms of a slightly anisobidentate dithiocarbamate ligand and to the two

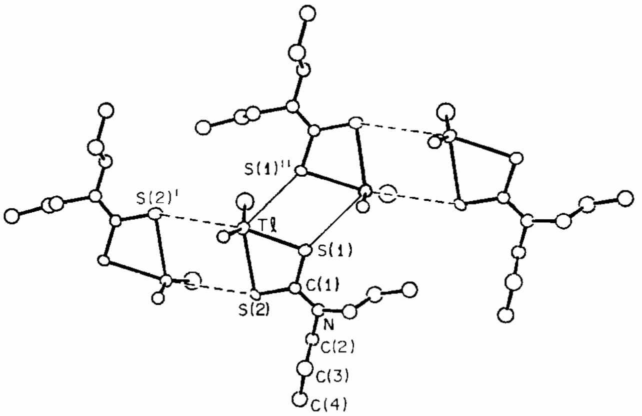


Fig. 1. The structure of [$TlMe_2(S_2CN^nPr_2)$] with the atom numbering scheme.

TABLE 3. Final atomic coordinates and isotropic temperature factors (Å^2)

Atom	*x/a*	*y/b*	*z/c*	B_{iso}
Tl	0.0190(1)	0	0.8029(1)	4.91(3)
S(1)	−0.0843(3)	−0.020(2)	0.4916(6)	5.6(2)
S(2)	−0.1320(2)	0.012(2)	0.7521(6)	4.6(1)
N	−0.2260(8)	0.033(3)	0.440(2)	4.5(3)
C(1)	−0.1553(9)	0.007(5)	0.550(2)	3.8(3)
C(2)	−0.288(1)	0.081(3)	0.483(3)	4.9(4)
C(3)	−0.331(2)	−0.066(4)	0.487(3)	7.3(4)
C(4)	−0.398(1)	−0.013(5)	0.527(3)	6.4(4)
C(2′)	−0.251(1)	−0.047(3)	0.267(3)	5.8(4)
C(3′)	−0.250(2)	0.097(4)	0.173(3)	6.8(4)
C(4′)	−0.266(1)	0.044(4)	−0.005(3)	6.4(4)
C(Me1)	0.033(1)	−0.239(3)	0.836(3)	4.0(4)
C(Me2)	0.060(2)	0.253(4)	0.860(4)	9.3(5)

TABLE 4. Interatomic distances (Å) and angles (°) around the Tl atom and in the ligand

Tl–S(1)	2.695(5)
Tl–S(2)	2.802(6)
Tl–C(Me1)	2.09(3)
Tl–C(Me2)	2.26(4)
Tl–S(2)'	3.704(5)
Tl–S(1)''	3.469(6)
S(1)–Tl–S(2)	64.8(3)
S(1)–Tl–C(Me1)	94.8(7)
S(1)–Tl–C(Me2)	109(1)
S(1)–Tl–S(2)'	169.7(2)
S(1)–Tl–S(1)''	62.0(2)
S(2)–Tl–C(Me1)	97.1(7)
S(2)–Tl–C(Me2)	104(1)
S(2)–Tl–S(2)'	105.2(3)
S(2)–Tl–S(1)''	126.9(3)
C(Me1)–Tl–C(Me2)	153(1)
C(Me1)–Tl–S(2)'	84.1(7)
C(Me1)–Tl–S(1)''	89.0(7)
C(Me2)–Tl–S(2)'	74(1)
C(Me2)–Tl–S(1)''	91(1)
S(2)'–Tl–S(1)''	127.9(2)
S(1)–C(1)	1.72(2)
S(2)–C(1)	1.71(2)
N–C(1)	1.33(3)
N–C(2)	1.50(3)
N–C(2′)	1.60(3)
C(2)–C(3)	1.53(4)
C(3)–C(4)	1.58(5)
C(2′)–C(3′)	1.51(4)
C(3′)–C(4′)	1.59(4)
Tl–S(1)–C(1)	90(1)
Tl–S(2)–C(1)	87(1)
C(1)–N–C(2)	123(1)
C(1)–N–C(2′)	117(1)
C(2)–N–C(2′)	117(1)
S(1)–C(1)–S(2)	118(1)
S(1)–C(1)–N	120(1)
S(2)–C(1)–N	121(1)
N–C(2)–C(3)	108(1)
C(2)–C(3)–C(4)	107(1)
N–C(2′)–C(3′)	98(1)
C(2′)–C(3′)–C(4′)	108(1)

Symmetry operations: ' $-x, y, 2-z$; '' $-x, y, 1-z$

methyl groups. One of the Tl–S distances is longer and the other shorter than the thallium–sulfur distances observed in diphenyl(diethyldithiocarbamato)thallium(III) [4], and both are longer than those found in tris(dimethyldithiocarbamato)thallium(III) [13]. Additional weak intermolecular interactions give rise to a well-ordered spatial arrangement (Figs. 1 and 2) differing markedly from that of diphenylthallium diethyldithiocarbamate [4]. In both these compounds there are secondary bonds between the metal and the sulfur atoms of neighbouring molecules but in the dimethylthallium derivative these weak interactions (Tl...S(1)'' = 3.469(6) Å) (see footnote to Table 4 for symmetry code), form pairs giving rise to loosely bonded 'dimers' (see the two central molecules connected by light lines in Fig. 1). Surprisingly [4, 14], the 'pseudobridging' sulfur atom has planar instead of pyramidal coordination geometry (the plane of best fit through Tl, C(1), S(1), S(2), Tl'', C(1)'', S(1)'' and S(2)'' has $\chi^2 = 328$), probably due to the weakness of the bridging interactions. Each thallium atom of the 'dimer' has another sulfur atom at a distance of 3.704(5) Å, close to the sum of the van der Waals radii, 3.76 Å [15] (dotted lines in Fig. 1). Although this long distance probably excludes significant bonding interaction, it is noteworthy that the plane of best fit through Tl, S(1), S(2), C(1), Tl', S(1)', S(2)', C(1)', Tl'', S(1)'', S(2)'' and C(1)'' has $\chi^2 = 486$. Thus the lattice can be described as an arrangement of strips formed by monomer units (Fig. 2), with the thallium atoms close to imaginary lines running approximately parallel to the *c* axis.

IR spectra

Table 5 lists the most significant bands in the IR spectra of the ligands and complexes. In the 3500–3000

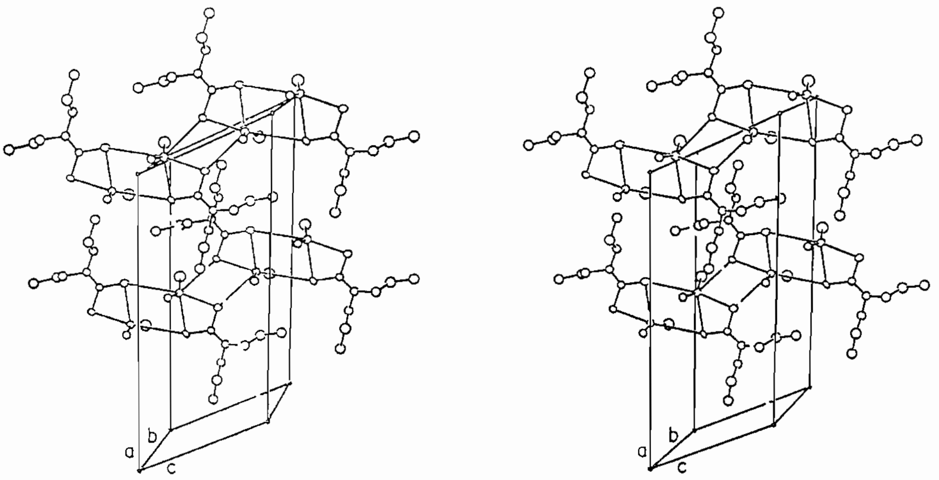


Fig. 2. ORTEP stereoview of the unit cell of $[TlMe_2(S_2CN^nPr_2)]$.

TABLE 5 Most significant IR bands of the ligands and complexes[a]

	ν(OH)	ν(NH)	ν(CN)	ν(CS)	$\rho(CH_3)$	ν_{asym}(C–Tl–C)	ν_{sym}(C–Tl–C)
$NaL^1\ 3H_2O$	3380s, b		1470vs	970vs			
$[TlMe_2L^1]$			1475vs	965vs	780m, b	520s	460m
$NaL^2\ 4H_2O$	3400s, b		1465vs	975vs			
$[TlMe_2L^2]$			1480vs	970vs	780m, b	510s	465s
$NaL^3\cdot 2H_2O$	3400s, b		1465vs	960vs			
$[TlMe_2L^3]$			1480vs	960vs	790m, b	520s	470s
$NaL^4\cdot 2H_2O$	3400s, b 3250s 3120s		1480vs	970vs			
$[TlMe_2L^4]$	3380vs		1480vs	950vs	790m, b	500s	475s
$NaL^5\cdot 2H_2O$	3400s	3200s 3100s	1525vs	955vs			
$[TlMe_2L^5]$		3200vs	1520vs	965vs	790m, b	530s	470m
$NaL^6\cdot 3H_2O$	3400s, b	3220s	1500vs	920vs			
$[TlMe_2L^6]$		3200vs	1510vs	930vs	790m, b	525s	465s

[a]b = broad; m = medium; s = strong; vs = very strong

cm^{-1} region the hydrated sodium salts of the ligands show the broad band typical of water; for ligand L^4 this band is complicated by the presence of an additional –OH group, and for L^5 and L^6 by N–H groups. The broad band disappears in all the complexes, but in $[TlMe_2L^4]$ ν(OH) emerges as a sharp band, as does ν(NH) in $[TlMe_2L^5]$ and $[TlMe_2L^6]$; this, together with the position of these sharp bands, suggests that the OH and NH groups of L^{4-6} are not involved in hydrogen bonds in their complexes.

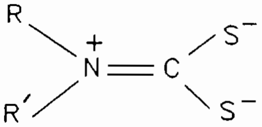
The C–N stretching vibration usually appears in dithiocarbamates as a strong band around 1500 cm^{-1}, a position indicative of a certain amount of double bond character (ν(C=N) = 1690–1640 cm^{-1}; ν(C–N) = 1350–1250 cm^{-1}[16]). This band is near this position in the sodium salts of the ligands used in this work, and shifts to slightly higher wavenumbers on coordination, revealing a slight increase in double bond character. The ν(C–S) band is located in the range 975–920 cm^{-1} in the sodium salts and appears as a single band near the same position in the complexes, which suggests only very slight modification of the C–S double bond character on complexation. According to the literature [17–20], the presence of a single ν(C–N) band at higher wavenumbers than in the free ligand, together with a single ν(C–S) band, suggests that in these complexes the dithiocarbamate ligand is bidentate or anisobidentate. This hypothesis is supported by the slightly anisobidentate character of the ligand shown by the X-ray diffraction study of [TlMe$_2$L^1]. As in other compounds [21], the presence of ligand bridges based on weak interactions does not complicate the ν(C–N) or ν(C–S) regions.

With respect to the organometallic part of the complexes, ρ(Me) , ν_{asym}(C–Tl–C) and ν_{sym}(C–Tl–C) have values close to those reported for other S,S-bonded dimethylthallium complexes [2, 3] in which the C–Tl–C fragment is slightly non-linear.

Conductivity and NMR spectra

The compounds are insoluble in water, but soluble in organic solvents of high permittivity such as DMSO, DMF and acetonitrile. [TlMe$_2$L^1] is also soluble in chloroform. According to their molar conductivities in acetonitrile (Table 1), they are all non-electrolytes in this solvent [22].

The most relevant ^{13}C NMR data for the L parts of [TlMe$_2$L^n] and NaL^n are listed in Table 6. The study of [TlMe$_2$L^1] included CP MAS ^{13}C NMR spectroscopy and measurements in CDCl$_3$ as well as in DMSO-d$_6$ solution. In the latter solvent the main spectral modification of the ligand signals upon coordination is the shielding of C(1), as is to be expected if coordination increases the contribution of the canonical form and the order of the C–N bond which is more shielding than the C=S bond [23]. Note that the position of the C(1) signal in DMSO-d$_6$ is similar for all the thallium compounds, suggesting that they have similar coordination schemes. Moreover, the chemical shift of C(1) for solid [TlMe$_2$L^1] is close to those observed in CDCl$_3$ and DMSO-d$_6$, suggesting that the main features of solid state coordination remain in the solution. The differences between the CP MAS and solution spectra of [TlMe$_2$L^1] concern the signals of the R groups, the magnetic non-equivalence of the C(4) methyl groups being shown by the splitting of the C(4) signal in the solid state spectrum.



The spectral parameters of the dimethylthallium unit are listed in Table 7 together with the corresponding

TABLE 6 ^{13}C NMR data for the ligand fragment^a

	C(1)		C(2)		C(3)		C(4)		C(5)	
	NaL	[TlMe$_2$L]	NaL	[TlMe$_2$L]	NaL	[TlMe$_2$L]	NaL	[TlMe$_2$L]	NaL	[TlMe$_2$L]
L^1	212.2	207.1 206.5^b 206^c	54 7	53.8 54.3^b 57^c	20 3	19.7 20.2^b 21^c	11 3	11.0 11 2^b 14^c, 13^c		
L^2	213.8	208.8	60.9	59.5	26 6	26 3	20.3	19.9		
L^3	212 3	206 9	52 7	51.9	29.4	28.6	20.1	19.6	14.1	13 6
L^4	213 7	^{d}	57 1	56.7	59.3	58.2	42 1	42.3		
L^5	213 9	208.7	41.1	40 2	14.1	13 4				
L^6	213.8	209 0	46.5	45 3	30 7	30.0	19.9	19.6	13.9	13 6

^{a}In DMSO-d$_6$ except where otherwise indicated, δ in ppm, referred to the solvent peak; numbering scheme similar to that of Fig. 1; for L^4 C(4) is the carbon of methyl group ^{b}In CDCl$_3$. ^{c}CP MAS. ^{d}This peak was not observed due to the low solubility of the compound.

TABLE 7. ^{13}C NMR data for the organometallic fragment^a

	Spectral conditions	L^1	L^2	L^3	L^4	L^5	L^6	L^b	L^c
δ(Tl–CH$_3$)	DMSO-d$_6$	21.6	21.6	21.5	^{d}	22.4	22 5		
	CDCl$_3$	19.7						22 9	26.8
	solid state	22							
^1J(^{13}C–Tl)	DMSO-d$_6$	2941	2952	2955	^{d}	2953	2959		
	CDCl$_3$	2450						2375	2268
	solid state	2511							

$^a\delta$ in ppm, referred to the solvent peak and to adamantane in CP MAS ^{b}L = Ph$_2$PCS$_2$$^-$, from ref. 2. ^{c}L = Ph$_2$PS$_2$$^-$, from ref 3. ^{d}Not observed, due to low solubility.

data for other 1,1-dithiolates that are soluble in $CDCl_3$.

The values of δ(Tl–Me) and $^{1}J(^{13}\mathrm{C}-^{205}\mathrm{Tl})$ are clearly smaller and larger, respectively, than those reported for $[\mathrm{TlMe_2(S_2CPPh_2)_2(THF)}]$ [2] and $[\mathrm{TlMe_2(S_2PPh_2)}]$ [3]. The values of δ(Tl–(C)–H) and $^{2}J(^{1}\mathrm{H}-^{205}\mathrm{Tl})$ appear to show the same trend (data not shown), though the differences are too small for certainty Although there have been few studies on the factors governing these parameters in dimethylthallium compounds [24, 25], there is strong evidence that both coupling constants increase when the donor strength of the solvent increases [24, 25], and it also seems that the methyl proton signal shifts upfield in more donor solvents [24]. The former trend has been explained [24] in terms of changes in the mean singlet–triplet excitation energy of the contact contribution to the coupling constant [25], and the latter in terms of induction effects. Even though there may be other contributing factors, such as changes in thallium hybridization (the C–Tl–C angle ranges from 153(1)° in the dithiocarbamate to 171.2° in the dithiophosphinate), the values in Table 7 suggest that dithiocarbamates are better donors towards $\mathrm{TlMe_2}^+$ than phosphinodithioformates and dithiophosphinates.

In DMSO-d_6 the methyl chemical shifts and $^{1}J(^{13}\mathrm{C}-^{205}\mathrm{Tl})$ coupling constants for all the new compounds are very similar which supports the conclusion that they have similar coordination schemes. The fact that the chemical shift and coupling constant for solid $[\mathrm{TlMe_2L^1}]$ are close to those measured in $CDCl_3$ solution again suggests that this solvent probably does not significantly affect the ligand–metal bond.

Supplementary material

Anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.

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