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ORIGINAL PAPER

Steric influence on *hapto* interactions in supramolecularly linked thallium dithiocarbamates

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Abstract Spectral and structural characterization of diallyl and dibenzyl dithiocarbamates of thallium(I) indicated increased thalliocarbon *hapto* interactions in dibenzyl dithiocarbamate due to increased steric effects. Proton magnetic resonance spectra of the compounds showed that the protons in the vicinity of the thioureide nitrogen are highly deshielded and the corresponding ^{13}C spectra showed large chemical shifts of the thioureide carbons due to decreased electron density. Cyclic voltammetry and bond valence calculations established that the oxidation number of thallium was +1. The Tl–S bond distances in both compounds did not vary significantly. η^1–Tl···C(S$_2$) supramolecular interactions were observed in both compounds. A nonclassical S···H bond (2.841 Å) was also observed in the dibenzyl compound. Aside from the two noncovalent interactions mentioned, additional *hapto* interactions such as Tl(1)S$_2\eta^1$Cη^1Cη^2C$_2$ and Tl(2)S$_2\eta^1$Cη^3C$_3$ were observed. Both compounds formed polymeric chains through *hapto* interactions.

Keywords Main group compounds · Thallium(I) · *Hapto* · Supramolecular · X-ray structure determination · NMR spectroscopy

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Introduction

Thallium, a group 12 element, shows interesting structural variations in its compounds and is useful in many biomedical applications. Neuronal activity in rats has been analyzed using thallium diethyldithiocarbamate [1]. The utilization of thallium(I) acetate in the TlAMG technique and the application of ^{201}Tl in single-photon emission computed tomography (SPECT) imaging in humans are well documented [2, 3]. Thallium compounds find use in the production of optical glasses, lenses for IR equipment, scintillation sensors, high-temperature superconductors, OLED materials, and related nanoparticles [4–7]. Dithiocarbamates are highly versatile ligands that interact with main-group metals and stabilize a variety of oxidation states in different coordination geometries [8, 9]. A limited number of Tl(I) and Tl(III) dithiocarbamates have been structurally characterized [10–25]. In the work described in the present paper, the synthesis and the spectroscopic and single-crystal X-ray structural characterization of [Tl(dadtc)]$_2$ (**1**) and [Tl(dbdtc)]$_2$ (**2**) (dadtc = diallyldithiocarbamate, dbdtc = dibenzyldithiocarbamate) were achieved. The characteristics of thalliocarbon *hapto* interactions and the steric effects of substituents on the supramolecular interactions that prevail in the compounds were analyzed.

Results and discussion

Electronic, fluorescence, and IR spectra

Charge-transfer transitions are observed with maximum intensity, and the characteristic absorption bands appear at around 437 nm for the complexes. Intraligand transitions for the dithiocarbamate are observed at around 280 nm.

Low-intensity fluorescence maxima are observed at 407 and 410 nm for the compounds.

In the IR spectra of the compounds, characteristic thioureide bands are observed at 1,462 and 1,489 cm^{-1} for **1** and **2**, respectively, indicating that the partially double-bonded polar thioureide resonance structures provide a smaller contribution than they do in transition metal compounds [26, 27]. The $\nu_{\mathrm{C-S}}$ band appears in the range 1,053–1,073 cm^{-1}.

^{1}H NMR and ^{13}C NMR spectral studies

For compound **1**, the ^{1}H NMR spectrum shows a signal due to α-CH_2 at 4.63 ppm. The β- and γ-protons are deshielded and appear in the ranges 5.85–5.95 ppm and 5.16–5.28 ppm, respectively. Chemical shifts for the thioureide carbon ($N^{13}CS_2$) were observed at 205.2 and 206.7 for compounds **1** and **2**, respectively, and serve as a fingerprint for the dithiocarbamate in the compounds [28, 29]. In compound **1**, the α-carbon appears slightly deshielded and is found at 54.75 ppm. However, the β- and γ-carbons are highly deshielded and appear at 132.0 and 117.9 ppm, respectively.

Cyclic voltammetry

A representative cyclic voltammogram of **1** is shown in Fig. 1, and compound **2** showed a similar reduction pattern. The reduction potentials are −1.136 and −1.013 V for **1** and **2**. The voltammograms are well-defined irreversible one-electron reduction processes. One-electron reduction processes for Tl^{+1} have been reported to occur in aqueous medium ($TlClO_4$) at −1.100 V [30, 31]. The characteristics of the reduction observed in the present study are similar to those reported in aqueous medium, although the coordination environments are different. The electrochemical process envisaged is $Tl^{+} + e^{-} \rightarrow Tl$. A small current observed at −0.60 V corresponds to the stripping of thallium. The observed cyclic voltammetric processes confirmed that the oxidation state of the thallium in the compounds is +1. Upon the application of a positive potential, no significant rise in current was observed for either compound, indicating that there was no observable oxidation to +3, probably due to the chemical instability associated with the electrochemically oxidized species.

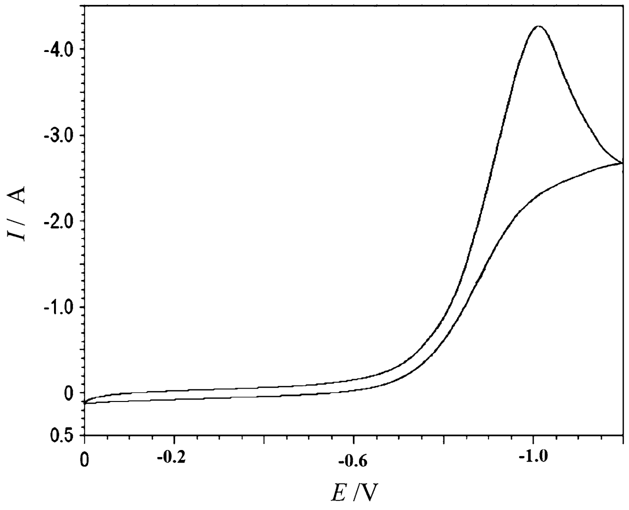

Fig. 1 Cyclic voltammogram of $[Tl(dadtc)]_2$

Crystal structures

Table 1 shows the data collection and refinement parameters and Table 2 shows important bond parameters of compounds **1** and **2**. An ORTEP diagram for $[Tl(dadtc)]_2$ (**1**) is shown in Fig. 2. In **1**, each thallium is primarily bonded to the two sulfur atoms of one dithiocarbamate with bond lengths of 2.968(2) and 2.988(2) Å. However, each thallium also shows nonbonded interactions with the two sulfurs of another (centrosymmetrically related) dithiocarbamate at distances of 3.165(2) and 3.287(2) Å, leading to a dimer (see Fig. 2). In addition, a fifth sulfur of the adjacent dithiocarbamate also shows a nonbonded Tl–S interaction at 3.506(2) Å. The dimer depicted in the ORTEP is part of the polymeric chain formed by the supramolecular interactions. The bond angle S–Tl–S between each thallium atom and the sulfur atoms that it is primarily bonded to is 59.46(5)°. The thioureide bond distance observed in the compound, 1.336(8) Å, clearly indicates the partially double-bonded nature of that bond. The four sulfur atoms in the dimer form a parallelogram, with the two thallium atoms occupying the axial positions. Effectively, each thallium is at the vertex of a pyramidal structure involving the two dithiocarbamates, considering the four relatively strong Tl–S interactions. The fifth sulfur occupies the apical position in the pyramid.

The ORTEP diagram of $[Tl(dbdtc)]_2$ (**2**) is shown in Fig. 3. Two formula units are present in the asymmetric unit of **2**. Each thallium is bound to two sulfurs of a dithiocarbamate unit at distances of 2.976(1) and 3.070(1) Å in one of the formula units (and at 2.960(1) and 3.046(1) Å in the other formula unit). In addition, thallium is bonded to two other sulfur atoms of another dithiocarbamate unit at distances of 3.053(1) and 3.167(1) Å in one formula unit (and at 3.098(1) and 3.214(1) Å in the other). The coordination environment around thallium is similar to that observed in **1**. The four sulfur atoms and thallium are arranged in an approximately pyramidal geometry. The thioureide C–N length in the molecule is 1.330(5) Å (or 1.348(5) Å in the other formula unit), which indicates its partially double-bonded nature. The bond angle S1–Tl1–S2 is 58.71(3)° (or 59.07(3)°) in the compound.

Table 1 Crystal data, data collection, and refinement parameters for **1** and **2**

	$[Tl(dadtc)]_2$ (**1**)	$[Tl(dbdtc)]_2$ (**2**)
Empirical formula	$C_{14}H_{20}N_2S_4Tl_2$	$C_{30}H_{28}N_2S_4Tl_2$
Formula weight	753.3	953.5
Dimensions/mm^3	0.32 × 0.09 × 0.08	0.14 × 0.12 × 0.05
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/_{C}$	P-1
a/Å	6.3136(6)	6.9562(5)
b/Å	18.1021(19)	12.6650(9)
c/Å	9.0382(9)	17.6744(12)
α/°	90.00	89.4864(11)
β/°	95.9554(18)	85.7503(11)
γ/°	90.00	76.6911(11)
V/Å^3	1027.40(18)	1511.08(18)
Z	2	2
D_{calc} /g cm^{-3}	2.435	2.096
μ/cm^{-1}	16.068	10.950
F (000)	688	896
λ/Å	0.71673	0.71073
Index ranges	$-7 \le h \le 7$; $-12 \le k \le 12$; $-11 \le l \le 11$	$-9 \le h \le 9$;$-18 \le k \le 18$; $-25 \le l \le 25$
Reflections	2,018	9,180
Reflections	1,665	6,206
Weighting scheme	$w = 1/[S^2 (F_o{}^2) + (0.0.492P)^2]$ where $P = (F_o{}^2 + 2 F_c{}^2)/3$	$w = 1/[\sigma^2(F_o{}^2) + 0.0397P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$
Parameters refined	100	343
Final R, R_w	0.0282, 0.0806	0.0606, 0.0846
Goof	1.050	1.003

Table 2 Selected bond distances/Å and bond angles/°

$[Tl(dadtc)]_2$		$[Tl(dbdtc)]_2$	
Tl1–S1	2.9679 (18)	Tl(1)–S(2)	2.976 (1)
Tl1–S2	2.9876 (19)	Tl(1)–S(1)	3.053 (1)
Tl1–S2′	3.1652 (18)	Tl(1)′–S(1)	3.070 (1)
Tl1–Tl1′	3.7256 (5)	Tl(1)′–S(2)	3.167 (1)
S1–C1	1.697 (6)	Tl(1)–Tl(1)′	3.6132 (4)
S2–C1	1.724 (6)	Tl(2)–S(4)	2.9603 (13)
N1–C1	1.336 (8)	Tl(2)–S(3)	3.0459 (14)
N1–C2	1.458 (8)	Tl(2)–S(4)	3.0982 (12)
N1–C5	1.465 (8)	Tl(2)–Tl(2)′	3.6962 (4)
C2–C3	1.472 (10)	S(1)–C(1)	1.727 (4)
S1–Tl1–S2	59.46 (5)	S(1)–Tl(1)–S(2)	56.91 (3)
S1–Tl1–S2′	81.19 (5)	S(1)–Tl(1)–S(2)	79.12(3)
S2–Tl1–S2′	105.53 (4)	S(4)–Tl(2)–S(3)	59.07 (3)
S1–Tl1–Tl1′	57.49 (4)	S(4)–Tl(2)–S(4)	104.85 (3)
S2–Tl1–Tl1′	54.94 (3)	S(3)–Tl(2)–S(4)	79.80 (3)
C1–S1–Tl1	89.3 (2)	C(1)–S(1)–Tl(1)	85.34 (13)

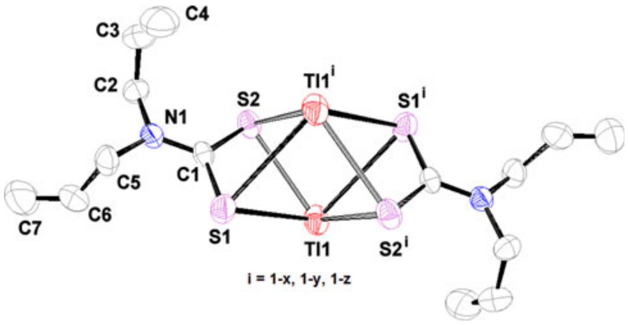

Fig. 2 ORTEP of $[Tl(dadtc)]_2$

Supramolecular interactions

$[Tl(dadtc)]_2$ (**1**) shows a Tl···C(S_2) *hapto* interaction, which occurs at a distance of 3.335 Å. An additional mono *hapto* interaction involving thallium is observed to occur at a distance of 3.469 Å with the carbon of the dithiocarbamate group of the next dimeric unit. The compound shows a supramolecularly linked polymeric chain which is

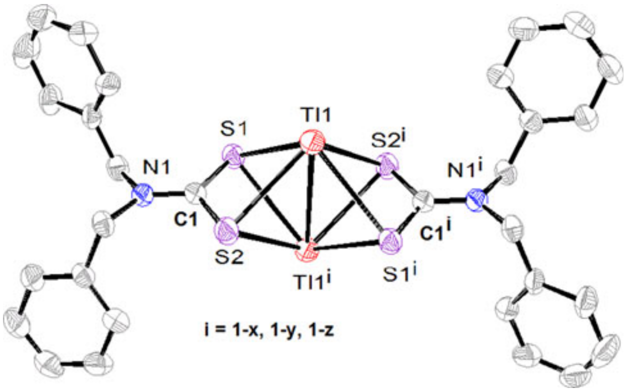

Fig. 3 ORTEP of $[Tl(dbdtc)]_2$

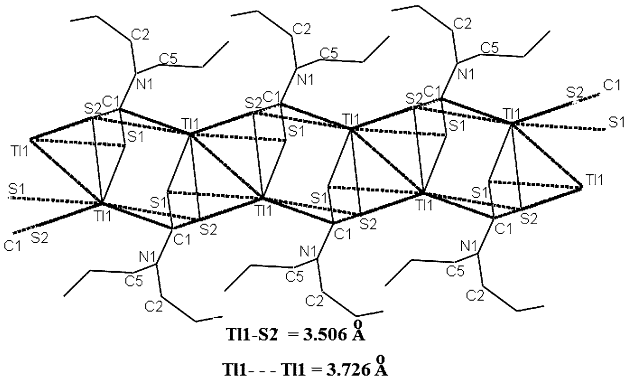

Fig. 4 Supramolecular interactions in $[Tl(dadtc)]_2$

connected via Tl1···S2 interactions (distance of interaction: 3.506 Å) and is stacked along the *a* axis, as depicted in Fig. 4.

The T12···Cl6 distance in one formula unit of **2** is 3.383 Å (or 3.412 Å in the other formula unit), which is significantly less than the sum of the van der Waals radii of Tl and C, 3.73 Å, indicating a significant *hapto* interaction. A nonclassical hydrogen-bonded S4···H5 interaction at a distance of 2.841 Å is observed (note that the sum of the van der Waals radii in this case is 3.0 Å). Tl2 shows a η^3 interaction with the benzene ring involving C3, C4, and C5 at distances of 3.656, 3.473, and 3.555 Å, respectively. T11 is also bound to two of the carbons (C22 and C23) of the second molecular unit through a *dihapto* (η^2) interaction at distances of 3.483 and 3.607 Å. The Tl···Tl distance in the dimer is 3.613 Å. Each dimer is flanked on either side by two other dimers, and this trimeric unit of dimers is held together by supramolecular interactions (η^3 involving C3, C4, and C5). Therefore, each thallium is directly bonded to two sulfur atoms of the dithiocarbamate, but is also bonded to two more sulfur atoms of the other dithiocarbamate at a longer distance. The two coordination environments may be described as $Tl1(S)_2\ \eta^1C\ \eta^1C\ \eta^2C_2$ and $Tl2(S_2)\ \eta^1C\ \eta^3C_3$, and the *hapto* interactions in the dimer are shown in Fig. 5. In the dimeric unit, the four sulfur atoms form a parallelogram and the thallium atoms occupy the apical positions of a bicapped parallelogram, as shown in Fig. 6. The axial distance between the thallium atoms in the dimeric unit reflects its stability.

Important structural parameters of the compounds are compared in Table 3. The Tl–S bond lengths in **1** and **2** barely change when different substituents are considered, though the dibenzyl analog shows an increasing bond length. In compound **1**, a weak supramolecular interaction prevails between thallium and hydrogen, leading to one of the shortest interaction distances reported so far (2.962 Å).

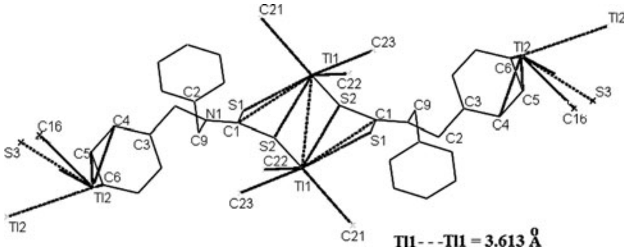

Fig. 5 Supramolecular interactions in $[Tl(dbdtc)]_2$

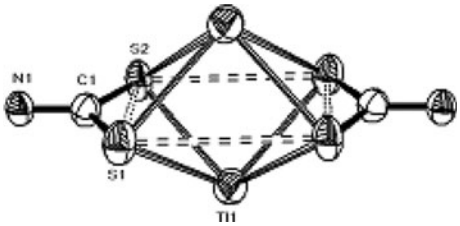

Fig. 6 Bicapped Tl_2S_4 parallelogram

η^1–Tl···C(S_2) supramolecular interactions are observed in both compounds. Perusal of the nonbonded distances indicates that the diallyl complex shows a relatively long Tl···Tl (3.726 Å) distance compared to that observed in **2** (3.613 Å), due to steric effects. A comparison of the distances associated with methyl and ethyl analogs reported previously [14] shows that the Tl···Tl distances in those analogs are shorter than those observed in **1** and **2**, indicating decreased stability due to increased steric effects. Bond valence sum (BVS) calculations yielded 1.1877 and 0.9664 as the valence sums for **1** and **2**, respectively [32]. The increased *hapto* interactions in **2** cause its relatively low BVS. These bond valence sums are in line with the crystal structures and the results of cyclovoltammetric studies of the compounds, confirming that the formal oxidation state of thallium is +1.

Table 3 Comparison of structural parameters

Complex	Bonded Tl–S/Å	Nonbonded Tl···S/Å	C–N thioureide/Å	S–C–S/°	Tl···Tl/Å	S···H	η^1–Tl···C(S$_2$)/η^2/η^3–Tl···C
[Tl (dadtc)]$_2$	2.968(2); 2.988(2)	3.165(2); 3.287(2); 3.506(2)	1.336(8)	119.4(3)	3.726	–	3.335, 3.469
[Tl (dbdtc)]$_2^a$	2.976(1); 3.070(1)	3.053(1); 3.167(1)	1.348(5)	118.9(2)	3.613	2.841	3.383, 3.636, 3.473, 3.555

[a] One set of parameters is given

Conclusions

An IR spectral investigation confirmed the important contribution of the thioureide bonds to the dithiocarbamate. NMR spectral data on diallyl and dibenzyl dithiocarbamates of thallium(I) showed that the protons and carbons in the immediate vicinity of the thioureide nitrogen are strongly affected by the bonding to thallium. CV and BVS calculations established that the formal oxidation state of thallium is +1. In the present study, a comparison of the nonbonded covalent interactions in **1** and **2** clearly showed increased thalliocarbon *hapto* interactions in the dibenzyl dithiocarbamate **2** analog due to the presence of bulky phenyl groups.

Experimental

All reagents and solvents employed were commercially available analytical grade materials and were used as supplied, without further purification. IR spectra were recorded on ABB Bomem (Quebec, Canada) MB 104 spectrometer (range: 4,000–400 cm^{-1}) as KBr pellets. Electronic spectra were recorded in ethanol on a Hitachi (Tokyo, Japan) U-2001 spectrometer. Fluorescence spectra were recorded in ethanol. To prevent any nonlinearity of the fluorescent intensity, 350 nm was chosen as the excitation wavelength. NMR spectra were recorded on a Bruker (Rheinstetten, Germany) 400 MHz spectrometer at room temperature using CDCl$_3$ as solvent.

Intensity data were collected at ambient temperature (295 K) on a Bruker SMART 1000 CCD diffractometer using graphite monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) [33]. Data were corrected for absorption using the SADABS program [34]. The structures were solved by direct methods using SIR97 [35], and were refined by full matrix least squares using SHELXL-97 [36]. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically. Molecular plots were drawn with ORTEP [37] and the noncovalent interactions were visualized with the Mercury software package [38].

Diallyldithiocarbamatothallium(I) [Tl(dadtc)]$_2$ (**1**, $C_{14}H_{20}N_2S_4Tl_2$)

Diallylamine (0.18 cm^3, 2 mmol) and 0.12 cm^3 carbon disulfide (2 mmol) in ethanol were mixed under ice-cold conditions (5 °C) to obtain a yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, an aqueous solution of 0.446 g TlF (2 mmol) was added with constant stirring. A pale yellow solid separated from the solution, which was filtered, washed with alcohol, and dried in air. Pale yellow solid; m.p.: 170 °C; yield 67 %; IR (KBr): $\bar{\nu}$ = 1,462 (thioureide C–N), 1,053 (C–S) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 4.63$ (α-CH$_2$), 5.85–5.93 (β-CH), 5.16–5.28 (γ-CH$_2$) ppm; ^{13}C NMR(CDCl$_3$): $\delta = 54.75$ (α-CH$_2$), 132.0 (β-CH), 117.9 (γ-CH$_2$), 205.2 (thioureide C–N) ppm.

Dibenzyldithiocarbamatothallium(I) [Tl(dbdtc)]$_2$ (**2**, $C_{30}H_{28}N_2S_4Tl_2$)

Dibenzylamine (0.39 cm^3, 2 mmol) and 0.12 cm^3 carbon disulfide (2 mmol) in ethanol were mixed under ice-cold conditions (5 °C) to obtain a yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, an aqueous solution of 0.446 g TlF (2 mmol) was added with constant stirring. A pale yellow solid separated from the solution, which was filtered, washed with alcohol, and dried in air. Yellow solid; m.p.: 164 °C; yield 72 %; IR (KBr): $\bar{\nu}$ = 1,489 (thioureide C–N), 1073 (C–S) cm^{-1}; ^{1}H NMR (CDCl$_3$): $\delta = 5.26$ (benzyl CH$_2$), 7.17–7.42 (aromatic) ppm; ^{13}C NMR (CDCl$_3$): $\delta = 54.73$ (benzylic CH$_2$), 206.7 (thioureide C–N).

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