Inorganica Chimica Acta 365 (2011) 480-483

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Supramolecularly linked linear polymers of thallium(I) dithiocarbamates: Steric influence on the supramolecular interactions of methyl and ethylcyclohexyl dithiocarbamates of thallium(I)

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ARTICLE INFO

Article history: Received 11 May 2010 Received in revised form 27 August 2010 Accepted 18 September 2010 Available online 29 September 2010

Keywords: Thallium Dithiocarbamates Thioureide Supramolecular Single crystal X-ray structure

ABSTRACT

Spectral and single crystal X-ray structural studies on $[Tl(mchdtc)]_2$ (1) and $[Tl(echdtc)]_2$ (2) (where mchdtc = methylcyclohexyldithiocarbamate and echdtc = ethylcyclohexyldithiocarbamate) were carried out. Both the synthesized complexes were characterized by UV–Vis, fluorescence, IR, ¹H and ¹³C NMR spectra. IR spectra of the complexes show the contribution of the thioureide form to the structures. Both compounds show weak fluorescence. The bond valence sums calculated for the complexes support the highly covalent nature of the Tl–S interactions. A Tl—H short interaction observed in the methyl analogue is totally absent in (2) because of the change in conformation of the cyclohexyl ring due to the introduction of ethyl group. Though the neighbouring non-bonded groups are flexible, thallium adjusts its thall-ophilic contacts to retain a hemisphere free for its pair of 's' electrons in the presence of a sterically demanding ethyl group.

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1. Introduction

Compounds of thallium show interesting structural and chemical properties. Thallium diethyldithiocarbamate is used for highresolution mapping of neuronal activity using noxious stimulation in rats and acoustic stimulation, intracortical microstimulation and pharmacological inhibition of neuronal activity with muscimol in Mongolian gerbils [1]. TIAMG technique is used in activitydependent neuronal Tl⁺ uptake in the brain after intraperitoneal injections of thallium(I) acetate [2]. The most dominant application of Tl⁺ is the use of ²⁰¹Tl for single photon emission computed tomography (SPECT) imaging in humans, in particular for imaging myocardial viability [3]. Thallium compounds find practical application in the production of optical glass, lenses for IR equipment and scintillation sensors, thallium containing complex oxides are used in production of high-temperature superconductor [4]. Metal-organic coordination polymers are attracting attention because of their potential use as functional materials [5]. Tl(I) metalloorganic compounds exhibit supramolecular interactions. The nature of such supramolecular interactions is predicted by investigating various ligand-thallium interactions [6]. Laser ablation is a well known method of laser processing, laser ablation of thallium(III) oxide is used for the production of related nanoparticles and thin

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films [7]. Chloro complex of thallium ions is largely related to the application of triplet emitters in organic light emitting diode (OLED) technology [8]. From an inorganic chemist's standpoint, dithiocarbamates are highly versatile ligands towards main group metals. They can stabilize a variety of oxidation states and coordination geometries and seemingly small modifications to the ligand can lead to significant changes in the structural behaviour of the complexes formed.

The structural parameters of the dithiocarbamate ligands themselves are not modified significantly on coordination to main group elements [9]. Tl(I) and Tl(III) dithiocarbamates have been structurally characterized [10–13]. The present work describes the synthesis, spectroscopic, single crystal X-ray structural characterization of [Tl(mchdtc)]₂ (1) and [Tl(echdtc)]₂ (2) [mchdtc = methylcyclohexyldithiocarbamate and echdtc = ethylcyclohexyldithiocarbamate]. Steric influence of the substituents on the supramolecular interactions prevailing in the compounds is analyzed.

2. Experimental

All the reagents and solvents employed were commercially available analytical grade materials and were used as supplied, without further purification. IR spectra were recorded on ABB Bomen MB 104 spectrometer (range 4000–400 cm⁻¹) as KBr pellets. The electronic spectra were recorded in ethanol on a HITACHI U-2001



Note



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Table 1	
Spectral data (NMR chemical shifts i	in ppm)

Complex	Uv–Vis nm	$IR (cm^{-1})$	NMR	α-CH	β -CH ₂	γ -CH ₂	δ -CH ₂	α' -CH ₃ /CH ₂	β' -CH ₃	$N^{13}CS_2$
(1)	434 ^a 407 ^b	1472 [*] 1077 ^{**}	¹ H ¹³ C	5.27(a) 61.67	1.81–1.88(e 30.34	e) 25.63–25.4	1.67–1.71(e) 8	3.43 35.05	-	- 202.4
(2)	434 ^a 411 ^b	1454* 1091**	¹ H ¹³ C	5.23(a) 62.26	1.81–1.91(e 31.02	e) 25.79	1.70(e) 25.49	3.90 42.98	1.30–1.36 14.76	- 202.0

* v_{C-N}.

** v_{C-S}.

^a CT.

^b Fluorescent bands excitation wavelength 350 nm.

Table 2

Crystal data, data collection and refinement parameters for [Tl(mchdtc)]₂ and [Tl(echdtc)]₂.

	[Tl(mchdtc)] ₂ (1)	[Tl(echdtc)] ₂ (2)
Empirical formula	$C_{16}H_{28}N_2S_4Tl_2$	$C_{18}H_{32}N_2S_4Tl_2$
Formula weight	785.4	813.4
Crystal dimension/mm	$0.24 \times 0.08 \times 0.07$	$0.17 \times 0.12 \times 0.10$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	6.2451(4)	6.6955(4)
b (Å)	18.6625(12)	15.4769(9)
<i>c</i> (Å)	9.6616(7)	12.3236(7)
β (°)	95.8057(12)	105.2202(10)
$U(Å^3)$	1120.28(13)	1232.25(12)
Ζ	2	2
$D_{\rm calc} ({ m g}{ m cm}^{-3})$	2.328	2.192
μ (cm ⁻¹)	14.741	13.405
F(000)	728	760
λ (Å)	0.71073	0.71073
Index ranges	$-7 \leqslant h \leqslant 7$; $-23 \leqslant k \leqslant 23$; $-11 \leqslant l \leqslant 11$	$-8 \leqslant h \leqslant 8; -18 \leqslant k \leqslant 18; -14 \leqslant l \leqslant 14$
Reflections collected	2214	2224
Observed reflections	1883	1871
R _{int}	0.058	0.055
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0447P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$	$W = 1/[\sigma^2(F_0^2) + (0.0586)^2]$ where $P = (F_0^2 + 2F_c^2)/3$
Number of parameters refined	110	119
Final R_1 , wR_2 (observed data)	0.0282, 0.0695	0.0397, 0.0894
Goodness-of-Fit(GOF)	1.001	1.059

spectrometer. Fluorescence spectra of the complexes were recorded in ethanol. To prevent any non-linearity of the fluorescent intensity, 350 nm was chosen as the excitation wavelength. NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature using CDCl₃ as solvent.

2.1. X-ray crystallography

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) [14]. All the nonhydrogen atoms were refined anisotropically and the hydrogen atoms were fixed geometrically. Details of crystal data, data collection and refinement parameters for (**1**) and (**2**) are summarized in Table 2.

2.2. Preparation of (disubstituted dithiocarbamato)thallium(I); $[Tl(R_1R_2dtc)]_2$

N-Methyl *N*-cyclohexylamine (2 mmol, 0.26 mL) in ethanol and carbon disulphide (2 mmol; 0.12 mL) in ethanol were mixed under ice-cold condition (5 °C) to obtain yellow dithiocarbamic acid solution. To the freshly prepared dithiocarbamic acid solution, an aqueous solution of TIF (2 mmol, 0.446 g) was added with constant stirring. A pale yellow solid separated from the solution, which was filtered, washed with alcohol and was dried in air. A similar procedure was employed for the preparation of the *N*-ethyl *N*-cyclohexylamine (2 mmol, 0.29 mL) analogue. Percentage of yield,

decomposition temperature and compositions for the two complexes are as follows: $[Tl(mchdtc)]_2$ (Yield: 65%; dec. 224 °C). *Anal.* Calc. for C₁₆H₂₈N₂S₄Tl₂ (785.38); C, 24.47; H, 3.60; N, 3.57. Found: C, 24.34; H, 3.20; N, 3.27%. And $[Tl(echdtc)]_2$ (Yield: 67%; dec. 194 °C). *Anal.* Calc. for C₁₈H₃₂N₂S₄Tl₂ (813.44); C, 26.58; H, 3.40; N, 3.44. Found: C, 26.27; H, 3.26; N, 3.21%.

3. Results and discussion

3.1. Infrared, electronic, fluorescence and NMR spectral studies

Spectral data for the compounds are shown in Table 1. The α -CH and α' -CH₃ protons are affected by the complexation to a maximum extent as a result of deshielding. In the cyclohexyl ring all the equatorial protons are deshielded to a large extent compared to the axial protons. Thioureide carbon shows the signal at 202.4 ppm in compound (**1**) and at 202.0 ppm in (**2**).

3.2. BVS calculation

For both the complexes, bond valence sums were calculated by summing up the bond valence contributions from five Tl–S and one Tl…C interactions [15]. The values are 1.2689 and 1.2897 for complexes (1) and (2) respectively. In the above complexes, the values are higher than the expected formal oxidation state of +1. The higher values observed in the present set of compounds support the fact that the Tl–S bonds are more covalent and the back bonding effects are very highly pronounced [16].

Table 3

Selected bond distances	(Å)	and bon	d angles	(°) for	compounds	(1)) and	(2)).
						composition		/		

1		2	
Tl(1)-S(1)	2.975(1)	Tl(1)-S(1)	3.078(2)
Tl(1)-S(1) ⁱ	3.086(1)	Tl(1)-S(1) ⁱⁱ	3.063(2)
Tl(1)-S(2)	3.162(1)	Tl(1)-S(2)	2.982(2)
$Tl(1)-S(2)^{i}$	3.165(2)	$Tl(1)-S(2)^{ii}$	3.164(2)
S(1)-C(1)	1.722(5)	S(1)-C(1)	1.720(6)
S(2)-C(1)	1.729(5)	S(2)-C(1)	1.730(6)
N(1)-C(1)	1.340(6)	N(1)-C(1)	1.340(7)
$S(1)-Tl(1)-S(1)^{i}$	106.52(3)	S(1)-Tl(1)-S(1) ⁱⁱ	106.89(4)
S(1)-Tl(1)-S(2)	57.59(3)	S(1)-Tl(1)-S(2)	58.38(4)
$S(1)^{i} - Tl(1) - S(2)$	81.00(3)	$S(1)^{ii} - Tl(1) - S(2)$	81.70(5)
$S(1)-Tl(1)-S(2)^{i}$	82.69(4)	$S(1)-Tl(1)-S(2)^{ii}$	78.61(4)
$S(2)-Tl(1)-S(2)^{i}$	110.05(3)	S(2)-Tl(1)-S(2) ⁱⁱ	107.02(4)
$C(1)-S(1)-Tl(1)^{i}$	86.20(15)	$C(1)-S(1)-Tl(1)^{ii}$	87.1(2)
$Tl(1)-S(1)-Tl(1)^{i}$	73.48(3)	Tl(1)-S(1)-Tl(1) ⁱⁱ	73.11(4)
C(1)-N(1)-C(8)	120.6(4)	C(1)-N(1)-C(8)	120.7(5)
C(1)-N(1)-C(2)	122.7(4)	C(1)-N(1)-C(2)	121.9(4)

Symmetry codes: (i) 1-x, 1-y, -z; (ii) 2-x, 1-y, 1-z.



Fig. 1. ORTEP diagram of $[Tl(mchdtc)]_2$ (30% probability level; i = 1 - x, 1 - y, -z).



Fig. 2. Linear polymeric chains of [Tl(mchdtc)]₂.

3.3. Structural analysis

Selected bond lengths and bond angles for (1) and (2) are given in Table 3. The ORTEP diagram of $[Tl(mchdtc)]_2$ is shown in Fig. 1. Tl(I) is bound to a single molecule of mchdtc by a short and a relatively long sulphur interaction measuring 2.9747(14) and 3.1621(14) Å. In addition, in the dimeric unit, it is also bound to the sulphurs of a centrosymmetrically-related mchdtc molecule at 3.086(1) and 3.165(2) Å. A weak interaction prevails between the Tl and C(1) atoms of the dithiocarbamate moiety at a distance



Fig. 3. Stacking of [Tl(mchdtc)]₂ in the unit cell.



Fig. 4. ORTEP diagram of $[Tl(echdtc)]_2$ (30% probability level: i = 2 - x, 1 - y, 1 - z).



Fig. 5. Linear polymeric chains of [Tl(echdtc)]₂.

of 3.428(4) Å. (the sum of the van der Waals radii for Tl and C is 3.73 Å) [16]. Interestingly, the Tl....Tl distance in the complex within a dimer is 3.626(5) Å, which is shorter than sum of the van der Waals radii (3.92 Å), suggesting the presence of a Tl....Tl interaction. Coordination of a bulky Tl(I) ion, results in the widening of the S–C–S angle to 118.2(3)° (normal angle ~109°). The widening of the angles enhances a stronger interaction between thallium and carbon atom in addition to the sulphurs. In the crystal packing, a long range interaction of 3.347(1) Å connects each thallium atom with a sulphur atom of an adjacent dimeric unit, forming one-dimensional polymeric chains along the crystallographic *a* axis involving supramolecular interactions (Fig. 2). The Tl–S–Tl angle within the chain is 152.21°. Stacking of the chains along the *c* axis reveals the presence of Tl…·H contacts (2.96 Å; Fig. 3), which are among the shortest reported so far [17].

The ORTEP diagram of [Tl(echdtc)]₂ is shown in Fig. 4. The coordination geometry of the metal is very similar to that observed in (1), with the thallium atom bound to two sulphur atoms of the same echdtc molecule at 2.982(2) and 3.078(2) Å and to two other sulphurs of a centrosymmetrically-related dithiocarbamate moiety at 3.063(2) and 3.164(2) Å. A relatively weak Tl....S interaction of 3.640(2) Å is observed. The Tl····C(1) and Tl····Tl separations within a dimer are 3.362(6) and 3.658(1) Å, respectively. The S-C-S angle of the dithiocarbamate is 118.0(3)°. As observed in (1), adjacent dimeric units are linked along the *a* axis into a one dimensional polymeric chain by Tl....S contacts (Fig. 5), where. Tl-S-Tl angle (159.46°) shows a slight increase with respect to the methyl analogue. In contrast with (1), no Tl....H short contacts are present among the chains because of the change in conformation of the cyclohexyl ring due to the introduction of ethyl group. Though the neighbouring non-bonded groups are flexible, thallium adjusts its contacts to retain a hemisphere free for its pair of s electrons in the presence of a sterically demanding ethyl group [18].

Appendix A. Supplementary material

CCDC 747993 and 747992 contain the supplementary crystallographic data for (1) and (2). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.09.029.

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