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Journal of Molecular Structure 656 (2003) 225–230

Journal of MOLECULAR STRUCTURE

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Supramolecular self-assembly of $Ph_2Tl(S_2COMe)$ based on a rare coordination mode of the xanthate ligand and thallium···π-phenyl interactions

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Received 18 March 2003; accepted 14 April 2003

Dedicated to Professor Achim Müller with great admiration for his spectacular contributions to supramolecular inorganic chemistry

Abstract

Diphenylthallium(III) xanthates, $Ph_2Tl(S_2COR)$, R = Me, Et, iso-Pr, Bz, have been prepared from Ph_2TlBr and KS_2COR, and the crystal structure of $Ph_2Tl(S_2COMe)$ has been determined by single crystal X-ray diffraction. The compound displays a supramolecular structure consisting of $Ph_2Tl(S_2COMe)$ tectons, self-assembled through intermolecular Tl···S and Tl···O secondary bonds and Tl···π-phenyl interactions.

Keywords: Supramolecular; Self-assembly; Crystal structure; Diphenylthallium; Xanthate; Thallium···π-aryl interactions; Secondary bonds

1. Introduction

The coordination chemistry of 1,1-dithiolates (phosphor-1,1-dithiolates [1], dithioarsinates [2], dithiocarbamates [3], and xanthates [4]) received a great deal of attention over the time and they still are an important class of ligands. All these display a great variety of coordination patterns and quite frequently the soft-metal derivatives self-assemble into supramolecular structures [5].

The xanthate ligands can be coordinated to metal atoms (Scheme 1) as monodentate (a), isobidentate (b) or anisobidentate (c). In rare cases additional metal–oxygen interaction (coordination) (d) is observed. Bimetallic bridging also occurs through sulfur atoms (e), but occasionally the oxygen atom may become involved (f).

We report here the synthesis and characterization of four new diphenylthallium xanthates. These compounds seemed attractive due to the remarkable structural diversity of organotallium compounds in

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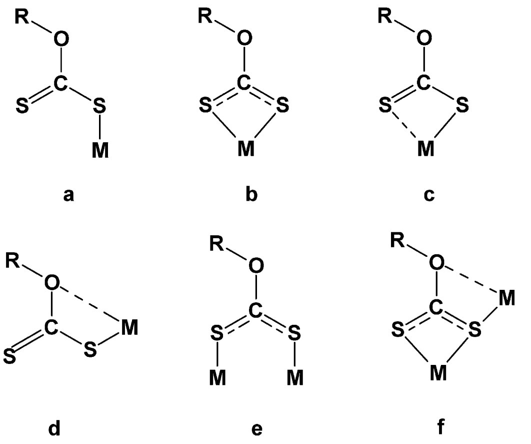
0022-2860/03/$ - see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S0022-2860(03)00344-2



Scheme 1. Some coordination patterns of xanthate ligands.

terms of coordination numbers and geometries and possible supramolecular self-assembly [6].

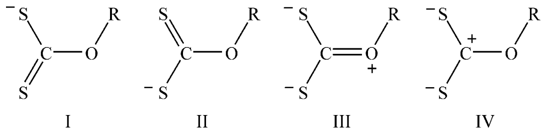
2. Results and discussion

2.1. Synthesis and characterization of the compounds

The compounds were prepared via metathetical reaction between one equivalent of diphenylthallium bromide with one equivalent of the corresponding potassium xanthate in methylene chloride suspension (Eq. (1)). The diphenylthallium xanthates, $Ph_2Tl(S_2COR)$, R = Me (**1**), Et (**2**), iso-Pr (**3**), Bz (**4**), are air-stable white solids, soluble in most common organic solvents.

$$Ph_2TlBr + KS_2COR \rightarrow Ph_2TlS_2COR + KBr \qquad (1)$$

The infrared absorption spectra of the xanthates and their metal complexes were extensively studied [7]. Qualitative studies, supported by normal coordinate analysis, revealed that within these systems (a xanthate ligand coordinated to a heavy atom) the vibrations are not pure. Their combination produce the so called 'xanthate bands' around 1260, 1120 and 1025 cm^{-1} [8], where the most important components are $\upsilon OC(S_2)$, $\upsilon_a CS_2$ and $\upsilon_s CS_2$, respectively. Furthermore, the position of these bands are strongly influenced by the contribution of the resonance forms I–IV to the overall structure.



These bands are useful in the characterization and, to some extent, prediction of the structure of the complex. For example, the presence of a band [$\upsilon OC(S_2)$], above 1200 cm^{-1} is an indication of a short $O-C(S_2)$ bond (form III has an important contribution), while the shift of that band to lower frequencies (below 1200 cm^{-1}) suggests that form III has a small contribution to the structure, leading to a rather long $O-C(S_2)$ bond. These suppositions are in good agreement with results observed in solid state, based on X-ray structural analyses [8,9].

As it can be seen in Table 1, only compound **4** has a band at 1224 cm^{-1}, suggesting contribution of form III. Its absence in compounds **1**–**3** can be correlated with a participation of oxygen in secondary bonding to the metal, as found by X-ray diffraction for compound **1** (vide infra).

2.2. Solid state structure of $Ph_2Tl(S_2COMe)$ (**1**)

Crystallization of **1** from methylene dichloride afforded X-ray quality crystals. Complete crystal structure analysis revealed that (**1**) displays a supramolecular structure consisting of $Ph_2Tl(S_2COMe)$ tectons [10], self-assembled through intermolecular Tl···S and Tl···O secondary bonds and Tl···π-phenyl interactions. The primary structure of

Table 1
Infrared spectral data for compounds (**1**)†(**4**)

1	**2**	**3**	**4**	Assignments[a]
1476m	1476m	1477s	1475w	$\delta_a O-CH_3$
1431m	1432m	1433s	1430m	$\delta_s O-CH_3$
–	–	–	1224m	$\upsilon OC + \rho CH_3 + \upsilon_a CS_2 + \upsilon_a CS_2$
1193s	1975vs	1197vs	1166vs	
1130s	1139m	1140s	1130sh	
1044s	1036w	–	1052vs	$\upsilon_s CS_2$
1020m	1020w	1021vs	1019w	$\upsilon CO + \upsilon_a CS_2$
966w	970s	968w	968m	$\upsilon_s COC + \upsilon_s CS_2$
690s	690s	694s	696s	$\upsilon_s CS_2 + \delta COC$

[a] The assignments listed here refer only to the major components.

the molecular tecton and the atom numbering scheme are presented in Fig. 1.

Selected bond lengths and angles are listed in Table 2. The molecular structure is based on an anisobidentate coordination mode of the xanthate ligand, the difference between the two sulfur–thallium distances [Tl–S(1) 2.845(3) Å and Tl–S(2) 3.001(2) Å] being around 0.2 Å. The phenyl groups have a deviation from linearity, the C(11)–Tl–C(21) angle being of 165.4(4)°.

The secondary structure, shown in Fig. 2, is the result of supramolecular self-assembly through intermolecular thallium–sulfur secondary bonds [Tl$\cdots$S(2a) 2.993(2) Å] with additional Tl$\cdots$O(1a) interactions (3.203(3) Å), leading to a zig-zag chain-like array running along the *b* axis of the crystal. These intermolecular distances are shorter than the corresponding van der Waals distances (Tl$\cdots$S 4.46 Å and Tl$\cdots$O 4.10 Å according to Batsanov [11]).

In the crystal the supramolecular chains are further associated through thallium$\cdots\pi$-phenyl interactions between adjacent chains, leading to a 2D stepped layered structure shown in Fig. 3. In this arrangement a phenyl group occupies the apparently empty space of an opposite thallium atom. It is noted that every second thallium atom in a chain is connected to a phenyl ring on the same side of a parallel chain. Intermolecular Tl$\cdots\pi$-phenyl interactions leading to supramolecular self-assembly have been previously observed in some thallium phenyl–pyrazolyl complexes and in other compounds [12].

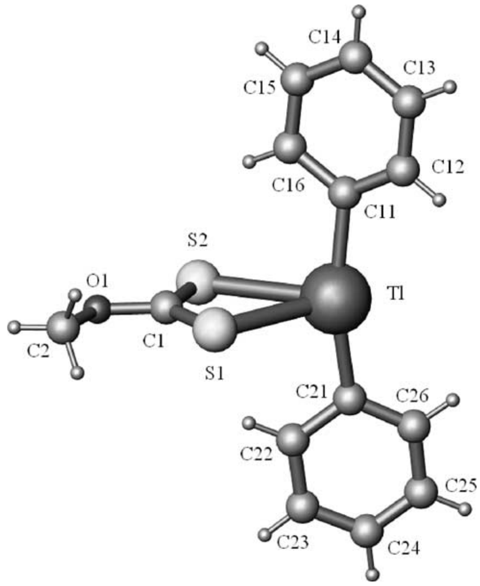


Fig. 1. Molecular structure of $Ph_2Tl(S_2COMe)$. Color scheme: thallium purple, carbon orange, sulfur yellow, oxygen red.

Table 2
Selected bond lengths and angles for (**1**)

Atoms	Distance	Atoms	Angles
Tl–S(1)	2.845(3)	S(1)–Tl–S(2)	61.12(7)
Tl–S(2)	3.001(2)	O(1a)–Tl–S(2a)	168.10(12)
Tl–S(2a)	2.993(2)	S(1)–Tl–S(2a)	81.83(7)
Tl(b)–O(1)	3.204(7)	Tl–S(2a)–Tl(b)	163.46(10)
Tl(b)–S(2)	2.993(2)	S(2a)–Tl(b)–S(2)	142.878(16)
Tl–C(11)	2.145(9)	S(1)–C(1)–S(2)	123.9(6)
Tl–C(21)	2.138(9)	C(11)–Tl–C(21)	165.4(4)
C(1)–S(1)	1.675(9)	O(1a)–Tl–S(2a)	48.59(12)
C(1)–S(2)	1.697(9)	C(21)–Tl–S(1)	96.7(3)
O(1)–C(1)	1.347(11)	C(11)–Tl–S(1)	97.8(3)
C(2)–O(1)	1.459(10)	C(21)–Tl–S(2)	92.2(2)
		C(11)–Tl–S(2)	95.3(2)
		C(21)–Tl–S(2a)	89.8(2)
		C(11)–Tl–S(2a)	91.7(2)
		C(11)–Tl–O(2a)	86.3(3)
		C(21)–Tl–O(2a)	83.8(3)

Symmetry transformations used to generate equivalent atoms: (a) $-x+1, y+1/2, -z+1/2$; (b) $-x+1, y-1/2, -z+1/2$.

In the molecular tecton (Fig. 1) the thallium atom is four-coordinate, with a ψ-trigonal bipyramidal geometry. If all the interactions are considered, the thallium atom becomes seven-coordinate (see Fig. 3) with a distorted pentagonal-bipyramidal geometry with axial phenyl groups, four equatorial positions occupied by three sulfur atoms and an oxygen atom. The π-aryl group occupies the fifth equatorial position, with the Tl$\cdots$centroid distance of 3.893 Å. This value is shorter than the sum of the van der Waals radius of thallium (2.46 Å) and the half-thickness of the phenyl ring (1.77 Å). The distance between the centroids of opposite (parallel) phenyl groups is 5.183 Å, too large for any significant π–π interaction.

The structure of our compound can be compared with that of $Me_2Tl(S_2COMe)$ [13]. The latter is also a supramolecular solid made of $Me_2Tl(S_2COMe)$ chelate molecular tectons (Tl–S 2.98(2) and 2.96(3) Å) with intermolecular contacts leading to a bidimensional layer made of interacting chain-like arrays (Tl$\cdots$S 3.19 Å, Tl$\cdots$O 3.13 Å within the chain). In

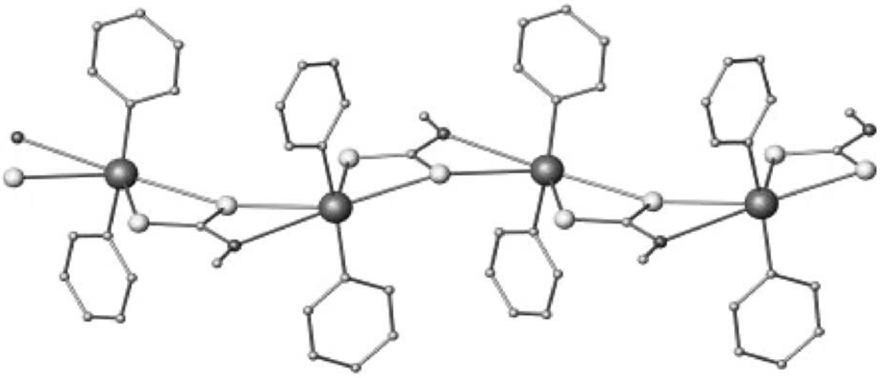


Fig. 2. Secondary structure formed by supramolecular self-assembly of (**1**).

this compound the chains are associated through Tl···S secondary bonds (interchain distances Tl···S 3.35 Å). The coordination geometry of seven-coordinate thallium is distorted pentagonal-bipyramidal, with axial methyl groups and the equatorial positions occupied by four sulfur atoms and an oxygen atom.

In both compounds $R_2Tl(S_2COR)$ the rare coordination pattern (f) is present, which involves a biconnective and a monoconnective sulfur atom and a monoconnective oxygen atom. Of the metal–ligand interactions in this pattern, two are secondary bonds (Tl···S and Tl···O).

A somewhat related structure is that of $Me_2Tl(OSPPh_2)$ [14], which involves ψ-trigonal-bipyramidal coordination of thallium, with four equatorial positions occupied by two sulfur and two oxygen

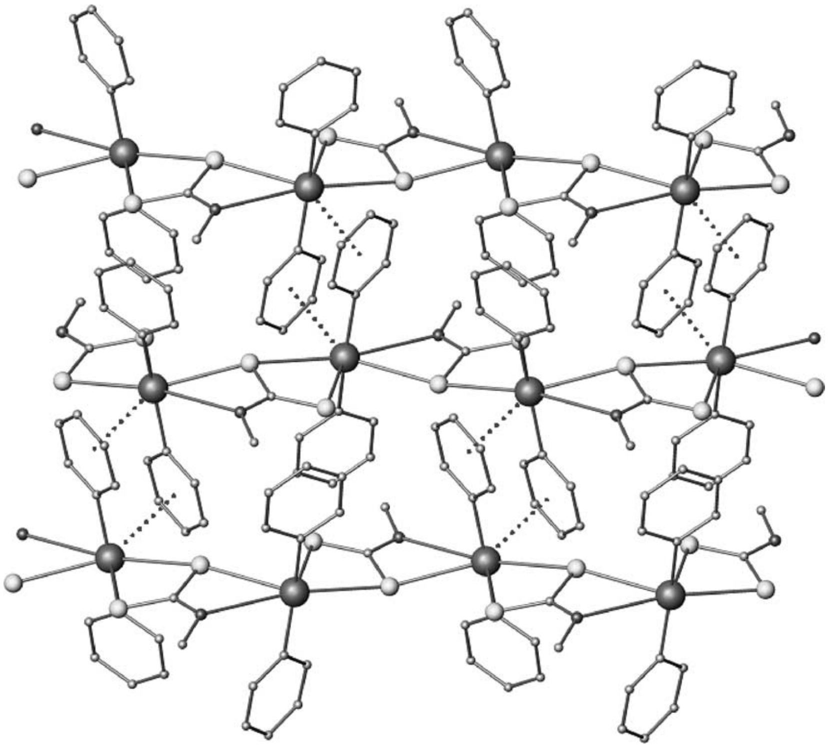


Fig. 3. Supramolecular 2D (layer) tertiary structure of (**1**) formed by Tl···π-phenyl inter-chain interactions.

atoms. In this structure, the chain-like arrays are not associated into a tertiary structure, probably because of the steric bulkiness of the phenyl groups.

3. Experimental

3.1. General

All reactions were carried out in open air. Elemental analysis was performed on a Perkin Elmer 240B apparatus. Melting points are uncorrected as determined on a Büchi apparatus. IR spectra were recorded on a Perkin Elmer 1330 spectrometer (KBr pellets). The starting material Ph_2TlBr was prepared as described in Ref. [15]; all solvents were commercial products of analytical grade purity (Aldrich) and used as supplied. Sodium methylxanthate or potassium benzylxanthate were prepared from the appropriate alcohol, sodium or potassium hydroxide and carbon disulphide, with excess alcohol acting as solvent. The synthesis of diphenylthallium methylxanthate is representative for all other syntheses in this work.

3.2. Synthesis of compounds

$Ph_2Tl(S_2COMe)$. To a suspension of Ph_2TlBr (0.439 g, 0.001 mol in 50 ml methylene chloride) was added a solution of NaS_2COMe (0.130 g, 0.001 mol in 50 ml ethanol). After 2 h of stirring the solution was filtered and concentrated under vacuum (ca. 10 ml) and petroleum ether (50 ml, b.p. 40–60 °C) was added to precipitate a white powder identified as $Ph_2Tl(S_2COMe)$ (yield: 51%, m.p. = 150 °C dec.). $C_{14}H_{13}OS_2Tl$ requires C, 36.10%, H, 2.81%, S, 13.77%; found C, 36.04%, H, 2.80%, S, 14.13%.

Similarly prepared were the following.

$Ph_2Tl(S_2COEt)$. Yield: 54%, m.p. = 150 °C dec. $C_{15}H_{15}OS_2Tl$ requires C, 37.55%, H, 3.15%, S, 13.37%; found C, 37.83%, H, 2.88%, S, 12.84%.

$Ph_2Tl(S_2COPr^i)$. Yield: 53%, m.p. = 190 °C dec. $C_{17}H_{19}OS_2Tl$ requires C, 40.21%, H, 3.77%, S, 12.63%; found C, 39.64%, H, 3.37%, S, 13.46%.

$Ph_2Tl(S_2COBz)$. Yield: 48%, m.p. = 145 °C dec. $C_{20}H_{17}OS_2Tl$ requires C, 44.33%, H, 3.16%, S, 11.84%; found C, 43.98%, H, 2.80%, S, 11.20%.

3.3. Crystallographic studies

A colorless prismatic crystal of $Ph_2Tl(S_2COMe)$ was grown by slow evaporation of a dichloromethane solution of the compound. The crystal was mounted on a glass fibber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in an Enraf Nonius MACH3 automatic diffractometer [16]. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω scan technique and corrected for Lorentz and polarization effects [17]. A semiempirical absorption correction (ψ scan) was made [18].

The structure was solved by direct methods [19] which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [20]. All hydrogen atoms were located from difference Fourier maps except those of the methyl groups which were located in their calculated positions (C–H = 0.96 Å). The located H atoms were refined isotropically, whereas the calculated H atoms were

Table 3
Crystal and structure refinement data for $(C_6H_5)_2Tl(S_2COCH_3)$ (**1**)

Empirical formula	$C_{14}H_{13}OS_2Tl$
Formula weight	465.73
Temperature (K)	293(2)
Wavelength	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.9426(17)
b (Å)	11.2339(11)
c (Å)	13.3300(20)
α (deg)	90
β (deg)	90.85(2)
γ (deg)	90
Volume (Å^3)	1488.7(4)
Z	4
Density (calc.) (Mg m^{-3})	2.078
Absorption coefficient (mm^{-1})	11.115
$F(000)$	872
Crystal size (mm^3)	0.35 × 0.25 × 0.10
Reflections collected	3733
Independent reflections	3582 [$R(int) = 0.0456$]
Data/restraints/parameters	3582/0/165
Goodness-of-fit on F^2	0.979
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0427$, $wR2 = 0.1041$
R indices (all data)	$R1 = 0.1027$, $wR2 = 0.1233$

refined using a riding model. A summary of the crystal data, experimental details and refinement results are listed in Table 3.

4. Supplementary material

Crystallographic information on (**1**) has been deposited with the Cambridge Crystalographic Data Center as supplementary publication number CCDC 208123. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank Xunta de Galicia (Spain) [Grant XUGA 20308 B 97] and the National Council for Academic Research (Roumania) [Grant No. 88] for the financial support of this work.

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