

Communication

# Tl<sup>I</sup>2D coordination polymer involving close Tl<sup>I</sup>···π (aromatic) contacts, [Tl<sub>3</sub>(μ-BPC)<sub>2</sub>(μ-NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub>

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Received 15 January 2006; received in revised form 24 April 2006; accepted 4 May 2006

Available online 11 May 2006

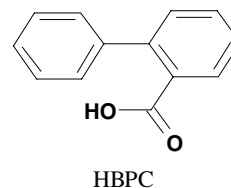
## Abstract

A two-dimensional polymer, [Tl<sub>3</sub>(μ-BPC)<sub>2</sub>(μ-NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> [BPC = biphenyl-2-carboxylate], has been synthesized and characterized. Its single-crystal X-ray structure shows three types of Tl<sup>I</sup>-ions with coordination numbers of 5 (Tl1 and Tl2), and 4 (Tl3). Two of the thallium atoms, Tl1 and Tl3, contain close Tl<sup>I</sup>···π (aromatic) contacts, thus attaining a total hapticity of 11 and 10 with environments Tl1O<sub>5</sub>C<sub>6</sub> and Tl3O<sub>4</sub>C<sub>6</sub>, respectively.

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**Keywords:** Biphenyl-2-carboxylic acid; Tl<sup>I</sup>···π interaction; Thallium; Crystal structure

Design and synthesis of new materials with specific properties and applications is a major challenge to chemists. Among all of the transition and non transition metals, Tl(I) chemistry is very interesting due to a variety of reasons. The Tl<sup>I</sup> compounds are interesting and frequently discussed in considering the “stereo-chemical activity” of valence shell electron lone pairs, potential ability to form metal–metal bonds and also complexes with aromatic hydrocarbons [1–32]. From recent structural study of Tl(I) complexes of anthranilates and salicylates [8], it has been argued that polyhapto-aromatic interactions also play an important role in determining the solid state lattices of such compounds, so that it was anticipated that this might be true for the Tl(I) complex of the biphenyl-2-carboxylate (BPC<sup>−</sup>). The “BPC<sup>−</sup>” anion with two aromatic groups and because of its ability for forming of polyhapto interactions may also be a good candidate for the investigation of the phenomena.



The reaction between “BPC<sup>−</sup>” and Tl<sup>I</sup>(NO<sub>3</sub>) provided colorless crystals with general formula [Tl<sub>3</sub>(μ-BPC)<sub>2</sub>(μ-NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> [HBPC = biphenyl-2-carboxylic acid] (1) [33]. Determination of the structure of the (1) by X-ray crystallography [34] showed three types of Tl<sup>I</sup>-ions with coordination numbers of 5 (Tl1 and Tl2) and 4 (Tl3) that are coordinated by oxygen atoms of biphenyl-2-carboxylate and nitrate anions with distances of ca. 2.63–2.95 Å (Fig. 1). The compound in solid state is a 2D polymer. The nitrate anion is disordered and acts as both a bidentate chelating, and a bridging group where two oxygen atoms coordinate to a thallium(I) ion and one these oxygen atom also as a bridge to another thallium atom, and the last oxygen atom only bridges to one thallium atom (Scheme 1a). The carboxylate group of the “BPC<sup>−</sup>” ligand acts only as

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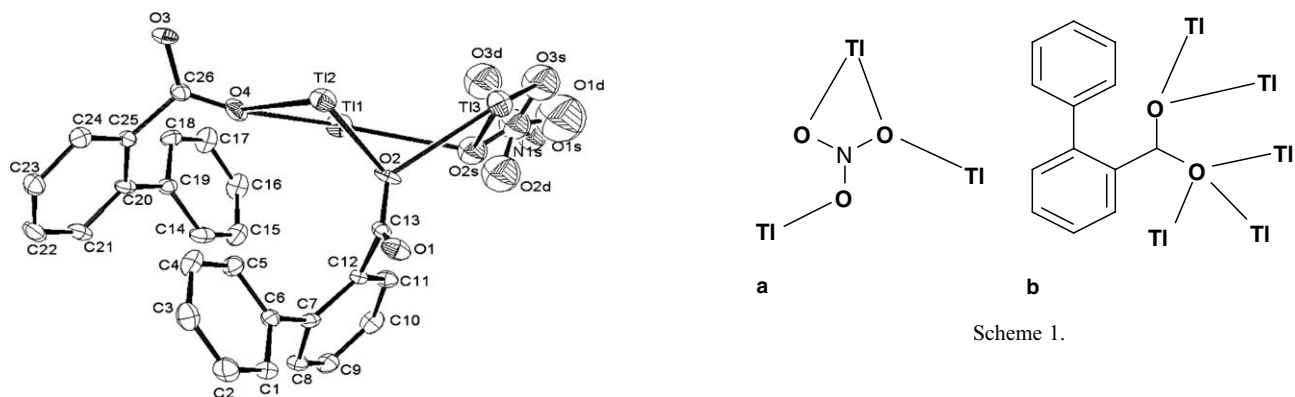


Fig. 1. ORTEP diagram of  $[\text{Ti}_3(\mu\text{-BPC})_2(\mu\text{-NO}_3)]_n$  (**1**), the nitrate anion is disordered.

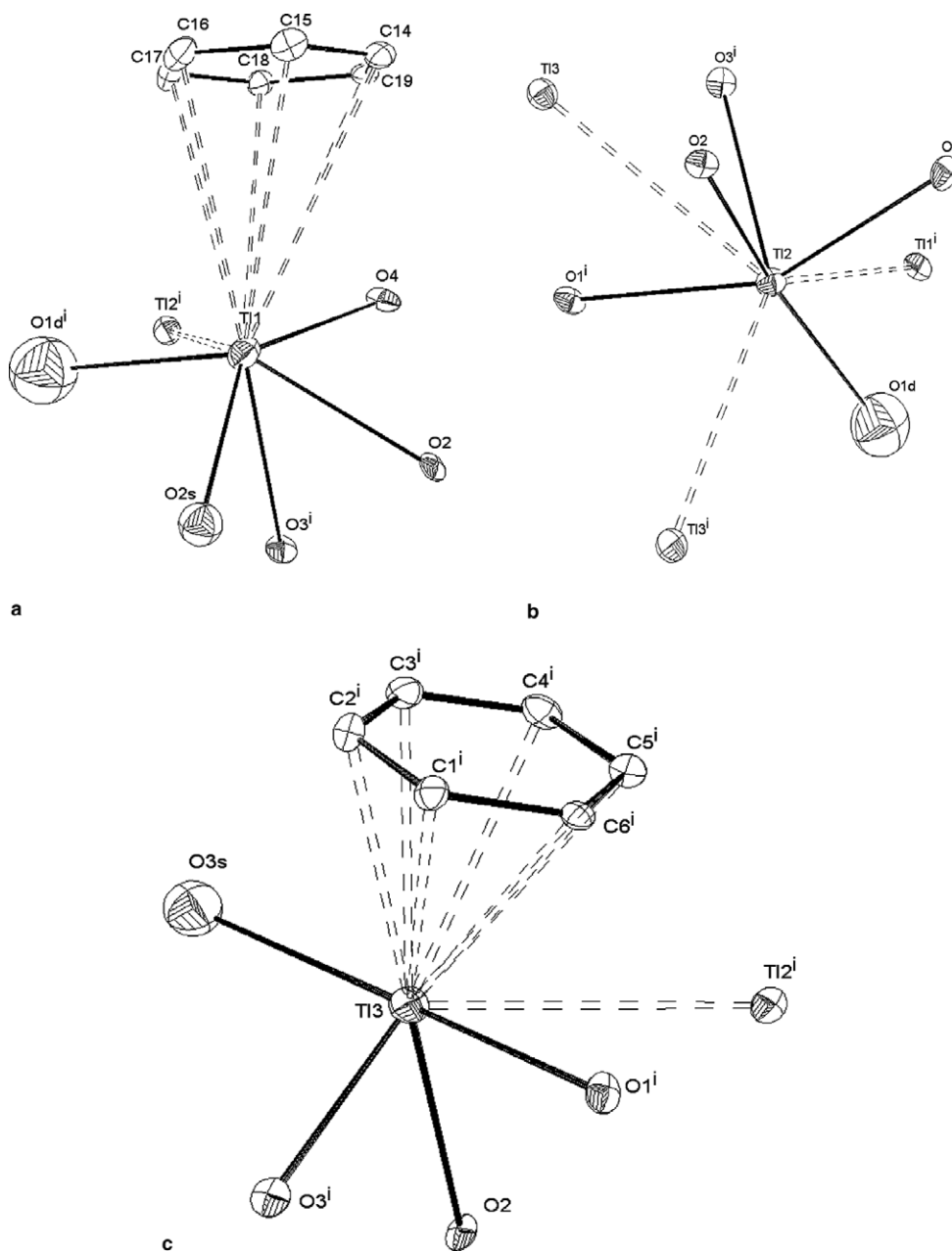


Fig. 2. Environment of Ti-atoms in  $[\text{Ti}_3(\mu\text{-BPC})_2(\mu\text{-NO}_3)]_n$  (**1**) after extending the bonding limit, showing of  $\text{Ti}\cdots\text{Ti}$  and  $\text{Ti}\cdots\text{C}$  interactions.

a bridging group where two oxygen atoms link to five thallium(I) ion, a novel and interesting behavior of a carboxylate group (Scheme 1b).

The arrangement of the O-atoms in this complex suggest a gap or hole in the coordination geometry around the Tl<sup>I</sup> coordination sphere (Fig. 2a–c), suggesting the lone pair of the Tl(I) atoms to be ‘active’ in the solid state [31,32].

With low coordination numbers of 4 and 5 for large thallium(I) ions in (1), one tends to look for secondary interactions that could possibly relieve this coordinative unsaturation. To find any other potential donor center, it is necessary to extend the bonding limit. A search was made generally for Tl $\cdots$ Tl and Tl $\cdots$ C approaches and it appears that Tl atoms may also be involved in thalophilic and polyhapto interactions. The separation between the thallium atoms is Tl1 $\cdots$ Tl2<sup>i</sup> = Tl2 $\cdots$ Tl1<sup>i</sup> = 3.906(7), Tl2 $\cdots$ Tl3 = 3.879(5), and Tl2 $\cdots$ Tl3<sup>i</sup> = Tl3 $\cdots$ Tl2<sup>i</sup> = 3.838(5) Å (Fig. 2a–c), which is less than twice the van der Waals radius of thallium (ca. 3.92 Å [33]) and was proposed to represent a weak attractive interaction.

A search was also made for Tl $\cdots$ C approaches and it appears that Tl1 and Tl3 in (1) may also be involved in close  $\eta^6$  interaction with one of phenyl groups of the “BPC<sup>−</sup>” ligand (Fig. 2a and c). Thus, the Tl1 and Tl3 atoms are linked to six carbon atoms of phenyl groups with distances Tl1 $\cdots$ C14, Tl1 $\cdots$ C15, Tl1 $\cdots$ C16, Tl1 $\cdots$ C17, Tl1 $\cdots$ C18 and Tl1 $\cdots$ C19 of 3.932, 3.802, 3.668, 3.668, 3.806, and 3.962 Å (with a Tl $\cdots$ centroid separation of 3.43 Å), respectively (Fig. 2a), and Tl3 $\cdots$ C1<sup>i</sup>, Tl3 $\cdots$ C2<sup>i</sup>, Tl3 $\cdots$ C3<sup>i</sup>, Tl3 $\cdots$ C4<sup>i</sup>, Tl3 $\cdots$ C5<sup>i</sup>, and Tl3 $\cdots$ C6<sup>i</sup> (*i*:  $-z$ ,  $-y$ ,  $-z$ ) of 3.812, 3.615, 3.444, 3.457, 3.658, and 3.830 Å (with a Tl $\cdots$ centroid separation of 3.32 Å), respectively (Fig. 2c). Hence, the Tl1 and Tl3 coordination sphere is completed and rather than a TlO<sub>5</sub> and Tl3O<sub>4</sub> coordination sphere, the complex can be considered to contain a hexahapto center with coordination numbers 11 and 10. The Tl $\cdots$ C separations range is 3.20–4.00 Å in recent reportedly species [8,26], and the sum of the van der Waals radii of C and Tl atoms is 3.66 Å [35]. Thus, hexahapto aromatic coordination of Tl1 and Tl3 appears to be yet another factor which can make varying contributions to the stability of complexes of this metal ion.

The obvious question then is whether the lone pair of the Tl1 and Tl3 atoms in (1) like that of Pb<sup>II</sup> [36] may or may not be involved in donor bonding with phenyl groups. Though a qualitative explanation of the nature of these particular interactions may be offered in terms of precise geometrical considerations, identification of the exact nature of the interaction is not always obvious [37]. Thus, whether the thallium atoms in (1) act only as a Lewis acid or whether as a Lewis acid and a Lewis base [37] is not clear.

#### Acknowledgement

Support of this work by the Tarbiat Modarres University is gratefully acknowledged.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.005.

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- [33] The complex [Tl<sub>3</sub>( $\mu$ -BPC)<sub>2</sub>( $\mu$ -NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> was prepared by dissolving 0.266 g (1 mmol) thallium(I) nitrate in distilled water and methanol and adding a mixture of biphenyl-2-carboxylic acid (0.198 g, 1 mmol) and potassium hydroxide (0.057 g, 1 mmol) in methanol. The resulting solution was stirred and then allowed to stand for some days at room temperature. Slow evaporation of the solvent at room temperature yielded crystals suitable for X-ray analysis (m.p. = 237 °C), Yield: 0.164 g (45%). The colorless crystals were washed with acetone and air dried. Anal. Calc. for C<sub>26</sub>H<sub>18</sub>NO<sub>7</sub>Tl<sub>3</sub>: C,

29.17; H, 1.68; N, 1.30; Tl, 57.22. Found: C, 28.80; H, 1.50; N, 1.50; Tl, 57.90%. IR (selected bands; in  $\text{cm}^{-1}$ ): 653w, 736m, 1384vs, 1432w, 1554vs, 3050w.  $^1\text{H}$  NMR (DMSO): 7.22–7.24(t, 1H), 7.25–7.27(t, 2H), 7.28–7.30(t, 2H), 7.31–7.34(t, 1H), 7.42–7.44(t, 2H), 7.47–7.49(t, 1H) ppm.  $^{13}\text{C}$ - $\{^1\text{H}\}$  NMR (DMSO): 126.37, 126.57, 127.41, 127.60, 127.76, 128.37, 129.57, 138.29, 142.15, 143.07 and 174.09 ppm.

[34] Crystallographic measurements were made at 293(2) K using a Bruker SMART 1000 CCD area detector [Bruker. Smart. Bruker Molecular Analysis Research Tool, Version 5.059. Bruker AXS, Madison, Wisconsin, USA, 1998b]. The structure was solved and refined with the program system SHELXTL [G.M. Sheldrick, Structure determination Software. SHELXTL. Version 5.10. Bruker. Bruker AXS, Madison, Wisconsin, USA, 1998b]. Intensity data were collected within the range  $3.00^\circ \leq \theta \leq 28.00^\circ$  with graphite monochromated Mo  $\text{K}\alpha$  radiation for a crystal of dimension  $0.16 \times 0.13 \times 0.12$  mm. Plots were prepared with ORTEP III [L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565]. Crystal data: formula,  $\text{C}_{26}\text{H}_{18}\text{NO}_7\text{Tl}_3$ ;  $M_r$

1069.53 g/mol; triclinic system, space group  $P\bar{1}$ ;  $a = 9.4299(17)$  Å,  $b = 10.1523(18)$  Å,  $c = 14.054(3)$  Å,  $\alpha = 82.796(5)^\circ$ ,  $\beta = 78.714(5)^\circ$ ,  $\gamma = 79.866(5)^\circ$ ;  $V = 1293.1(4)$  Å<sup>3</sup>;  $D_c = 2.747$  Mg/m<sup>3</sup> ( $Z = 2$ );  $F(000) = 960$ ;  $R(wR) = 0.0516$  (0.1077) for 3799 reflections, with  $I > 2\sigma(I)$ ;  $R(wR) = 0.0825$  (0.1163) for all data. The crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-295069. Copies of the data can be obtained, free of charge, by application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: data\_request@ccdc.cam.ac.uk, or via the internet (<http://www.ccdc.cam.ac.uk/products/csd/request>).

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