

Communication

# Highly polyhapto–aromatic interactions in thallium(I) coordination

Kamran Akhbari, Ali Morsali \*

*Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Islamic Republic of Iran*

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## Abstract

In the solid state, the Tl(I) complex of 4-hydroxybenzoate ( $\text{HB}^-$ ),  $[\text{Tl}(\text{HB})]_n$  (**1**), can be regarded as containing polymeric chains linked through  $2 \times \eta^6$  interactions of the Tl atoms with phenyl groups from adjacent units. The thallium atoms contain close  $\text{Tl}^I \cdots \pi$  (aromatic) contacts, thus attaining a total hapticity of 16 with environments  $\text{TlO}_4\text{C}_{12}$ . The unusually high coordination number in the this compound may reflect the capacity of Tl(I) to act as both a Lewis acid and a Lewis base.

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**Keywords:** Thallium(I); 4-Hydroxybenzoate; Polyhapto interaction; Lone pair

The  $\text{Tl}^I$  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]. From recent structural study of Tl(I) complexes of anthranilates, salicylates [2], and modified poly(pyrazolyl)borate ligands [3], it has been argued that polyhapto–aromatic interactions also play an important role in determining the solid state lattices of such compounds. Continuing with our previous work on  $\text{Tl}^I$  coordination polymers [4–11], we have now determined the structure of thallium(I) complex with the ligand 4-hydroxybenzoate ( $\text{HB}^-$ ), that provides a two-dimensional polymer construction of polyhapto–aromatic interactions and hydrogen bonds, interestingly, show the strong ability of  $\text{Tl}^I$  for forming of polyhapto interactions. Although discussions of compound **1** and similar compounds that describe primarily vibrational studies of thallium carboxylates and focus on the  $\text{Tl}^I\text{–O}_2\text{CR}$  interaction could be found in the literature [12–15], but no structural studies were done for compound **1**. We also should mention that the structural study of 2-hydroxybenzoate(salicylate) [9,16] and 3-hydroxybenzoate [17] were done and structure of compound **1** is as similar as thallium(I) salicylate, addition of

methyl groups to hydroxybenzoate were studied by Wiesbrock and Schmidbaur [2] and Olof Kristiansson [16].

The reaction between 4-hydroxybenzoic acid and  $\text{Tl}^I(\text{NO}_3)$  provided crystalline materials of the general formula  $[\text{Tl}(\text{HB})]_n$  (**1**) [18]. Determination of the structure of the compound **1** by X-ray crystallography [19] showed the complex to be a novel two-dimensional polymer.

There are four ( $\text{TlO}_4$ ) coordinate Tl atoms with distances of  $\text{TlI}^I\text{–O1} = 2.556(4)$ ,  $\text{TlI}^I\text{–O1}^{\text{iii}}$  (iii:  $-x, -y, -z$ ) =  $2.792(4)$ ,  $\text{Tl}^I\text{–O2} = 2.810(3)$ ,  $\text{Tl}^I\text{–O3} = 3.005(3)$  Å (Fig. 1). Each  $\text{HB}^-$  anion has four bonding interactions and four lone pairs of  $\text{HB}^-$  connect to three  $\text{Tl}^I$  ions. The carboxylate groups of the  $\text{HB}^-$  ligand act as both bidentate chelating, and bridging group where two oxygen atoms of the carboxylate group coordinate to a thallium(I) ion, also one of this oxygen atoms bridge to two other thallium atoms. The phenolic oxygen atom only link to one thallium atom. The oxygen atoms of carboxylate group and hydrogen atom of  $-\text{OH}$  groups of 4-hydroxybenzoate ( $\text{HB}^-$ ) anions in compound **1** are involved in a hydrogen bonding network (Fig. S2).

In compound **1**, the lone pair of Tl(I) is ‘active’ in the solid state. However, the arrangement of O-atoms suggest a gap or hole in coordination geometry around the Tl(I) coordination sphere (Fig. 1), a gap possibly occupied by a ‘stereo-active’ electron lone pair. Hence, the geometry of the nearest coordination environment of every Tl(I)-atoms is likely to be caused by the geometrical constraints

\* Corresponding author. Tel.: +98 2188011001; fax: +98 2188011101.  
E-mail address: [morsali\\_a@yahoo.com](mailto:morsali_a@yahoo.com) (A. Morsali).

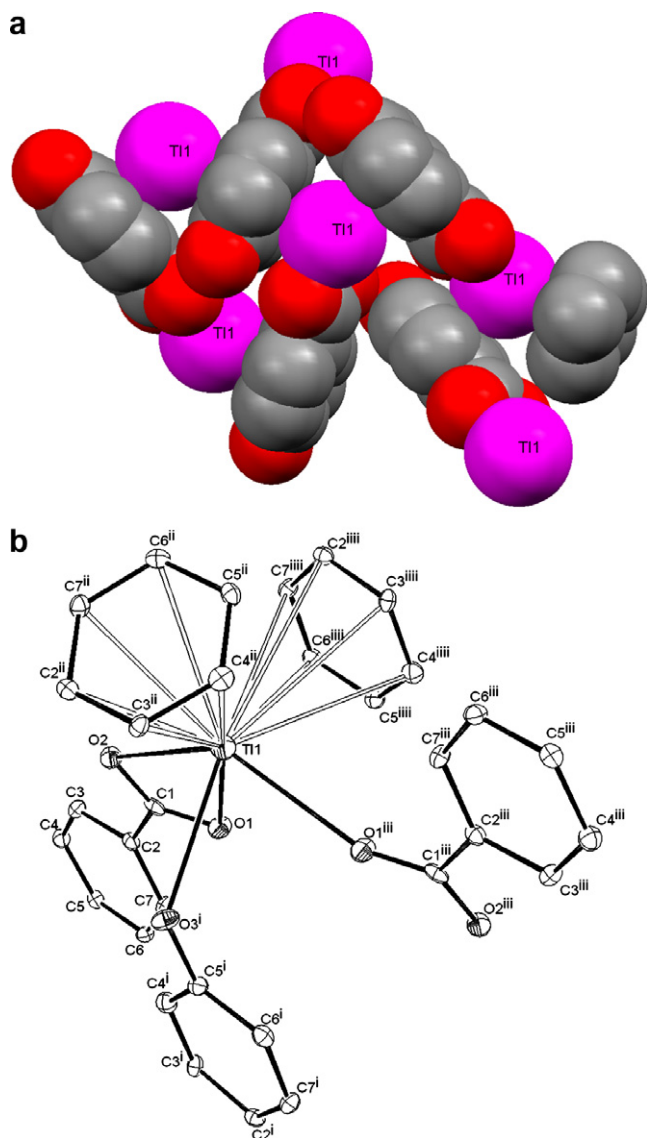


Fig. 1. (a) Space-filling representation, close approaches of Tl to the face of two phenyl rings can be seen. (b) Environment of Tl-atoms in compound **1** after extending the bonding limit, Tl...C interactions. (i)  $-x, y + 1/2, -z + 1/2$ , (ii)  $x + 1/2, -y + 1/2, -z$ , (iii)  $-x, -y, -z$ , (iv)  $x, -y + 1/2, z + 1/2$ .

of coordinated O-atoms, and by the influence of a stereochemically 'active' electron lone pair.

With low coordination number of 4 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...C approaches and it appears that Tl in **1** may also be involved in an  $2 \times \eta^6$  interactions with the phenyl groups of neighboring molecules (Figs. 1b, 2 and S1). Thus, the Tl(I) atoms are linked to 12 carbon atoms of phenyl groups (Table 1). The Tl...C6(plane) and the interplanar angle of the two phenyl groups surrounding the Tl-atom are 3.287(3) Å and 151.60(3)°, respectively, this Tl...C6(plane) value is similar to that of 3.27 Å in

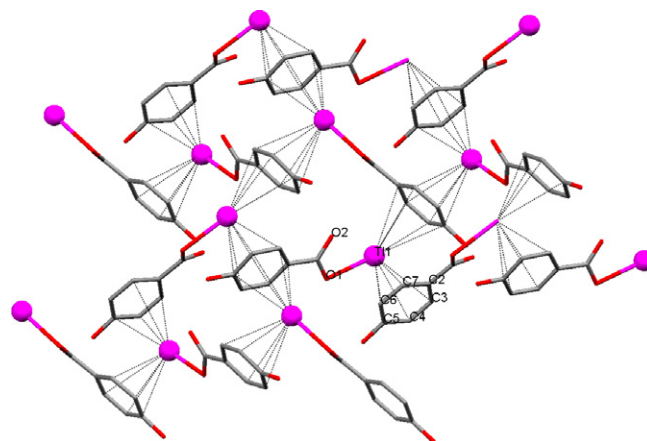


Fig. 2. A fragment of the two-dimensional layer in compound **1**, showing the  $\pi \cdots \text{Tl} \cdots \pi$  and  $\text{Tl} \cdots \pi \cdots \text{Tl}$  interactions. H atoms are omitted for clarity.

Table 1  
Distances of thallium(I) with carbon atoms of phenyl groups in compound **1**

Tl...C2 <sup>ii</sup>	3.554(2)	Tl...C2 <sup>iii</sup>	3.695(5)
Tl...C3 <sup>ii</sup>	3.487(2)	Tl...C3 <sup>iii</sup>	3.579(2)
Tl...C4 <sup>ii</sup>	3.487(2)	Tl...C4 <sup>iii</sup>	3.492(2)
Tl...C5 <sup>ii</sup>	3.575(3)	Tl...C5 <sup>iii</sup>	3.500(2)
Tl...C6 <sup>ii</sup>	3.688(5)	Tl...C6 <sup>iii</sup>	3.552(3)
Tl...C7 <sup>ii</sup>	3.654(2)	Tl...C7 <sup>iii</sup>	3.658(5)

((ii)  $x + 1/2, -y + 1/2, -z$  and (iii)  $-x, -y, -z$ ).

[Tl(PhNNPh)<sub>2</sub>], 3.33 Å in [Tl(TolNNTol)]<sub>2</sub> [17] and 3.29 Å in *catena*-[bis(μ<sub>3</sub>-salicylato)dithallium(I)] [16]. Hence, the Tl(I) coordination sphere is completed and rather than a TlO<sub>4</sub> coordination sphere, the complex can be considered to contain a  $2 \times \eta^6$  (C<sub>12</sub>O<sub>4</sub>Tl) center with a 16 coordination number, this coordination number and this structural behavior were exactly observed in thallium(I) salicylate [9,16]. The reported Tl...C separations range is 3.20–4.00 Å in recent reported species [2,20] and the sum of the vander Walls radii of carbon and Tl atoms is 3.66 Å [21]. Thus,  $2 \times \eta^6$  aromatic coordination of Tl(I) appears to be yet another factor which can make varying contributions to the stability of complexes of this metal ion.

However, the Tl<sup>I</sup> is one of the post-transition metal elements that exhibit "inert-pair effect", referring to the resistance of the pair of outer electrons on Tl(I) to removal or to participation in covalent bond formation or hydrogen bonding. The obvious question then is whether the lone pair in the Tl<sup>I</sup> of the compound **1** may or may not be involved in donor bonding. 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 and however, the distinction here of acceptor *vs.* donor is perhaps artificial. Actually, whether the thallium atoms in **1** act only as a Lewis acid or whether

as both a Lewis acid and a Lewis base is not clear and answer to this question definitively for compound **1** would require a computational study of the electron density or a high resolution charge density study. Since somewhat surprisingly, the recent report of polyhapto–aromatic interactions in lead(II) coordination suggested that the active lone pair in the Pb(II) may be involved in donor bonding [22]. Comparison with this reported Pb(II) compound [22] and because of the following reasons it may strongly be reflected that Tl(I) may be had higher capacity than Pb(II) to act as a *Lewis* base.

1. The higher polyhapto interactions for Tl atoms in the reported compound here than the Pb compound [22], coordination sphere of Tl(TlO<sub>4</sub>C<sub>12</sub>) in compound **1** compared with Pb(PbO<sub>5</sub>C<sub>8</sub>) reported recently [22].
2. The shorter M... $\pi$  for Tl atoms in the reported compound here than the Pb compound [22], Tl... $\pi$  = 3.287(3) Å compare to Pb... $\pi$  = 3.408(3) Å from the centroid of the phenyl groups.
3. The lower oxidation number +1 for Tl atoms compare to +2 for Pb atoms in the reported Pb compound [22].

However structural determination of compound **1** show two factors, hydrogen bonding and polyhapto interactions that may control the packing of this compound.

In order to examine the thermal stability of the compound **1**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 30 and 700 °C. Compound **1** does not melt and is stable up to 185 °C at which temperature it begins to melt and the decomposition of 4-hydroxybenzoate (HB<sup>−</sup>) anions take place at 200–420 °C with one endothermic and two exothermic effects at 245, 320 and 395 °C, respectively. The solid residue formed at around 420 °C is thus suggested to be Tl<sub>2</sub>O, (Fig. S3).

In spectrophotometric procedure, 2.0 ml of ligand solution (2.5 × 10<sup>−5</sup> M), after deprotonate the carboxylic acid group of H<sub>2</sub>B with KOH, in methanol was placed in the spectrophotometer cell and the absorbance of solution was measured. Then a known amount of the concentrated solution of thallium(I) nitrate in methanol (1.3 × 10<sup>−3</sup> M) was added in a stepwise manner using a 5- $\mu$ l Hamilton syringe. The absorbance spectrum of the solution was recorded after each addition. The thallium(I) ion solution was continually added until the desired metal to ligand mole ratio was achieved. The electronic absorption spectra of the ligand 4-hydroxybenzoate (HB<sup>−</sup>) in the presence of increasing concentration of thallium(I) ion in methanol at room temperature are shown in Fig. S4. As is obvious, the strong absorption of ligand at 267.2 nm, which is related to  $\pi \rightarrow \pi^*$  transition, increases with increasing concentration of the metal ion. The resulting absorbance against [Tl<sup>+</sup>]/[HB<sup>−</sup>] mole ratio plot, shown in the inset of Fig. S4, revealed an inflection point a metal-to-ligand molar ratio of about 1, emphasizing the formation of a 1:1 complex in solution. The formation and stoichiometry of

the Tl<sup>+</sup>–HB<sup>−</sup> complex in methanol solution was also investigated by a conductometric method. Twenty milliliters of thallium(I) nitrate solution (5.0 × 10<sup>−5</sup> M) in methanol was placed in a two-wall thermostated glass cell, the temperature was adjusted to 25.00 ± 0.05 °C, and the conductance of solution was measured. Then a known amount of the concentrated solution of ligand (HB<sup>−</sup>) in methanol (5.0 × 10<sup>−3</sup> M) was added in a stepwise manner using a 5- $\mu$ l Hamilton syringe. The conductance of the solution was measured after each addition. The ligand solution was continually added until the desired ligand to metal ion mole ratio was achieved. The conductivity of a 5.0 × 10<sup>−5</sup> M solution of thallium nitrate solution in methanol was monitored as a function of [HB<sup>−</sup>]/[Tl<sup>+</sup>] mole ratio at 25.00 ± 0.05 °C and the resulting plot is shown in Fig. S5. As it is seen, addition of the ligand to the metal salt solution then causes a increase in the solution conductivity possessing an inflection point at a molar ratio of about one, indicating the formation of a 1:1 Tl<sup>+</sup>–HB<sup>−</sup> complex in solution.

For evaluation of the conditional formation constants, the mole ratio data obtained by the two different physico-chemical methods employed were fitted to the previously reported equations [23,24] using a non-linear least-squares curve fitting program KINFIT [25]. The conditional formation constants of the complex were evaluated as 0.36 ± 0.01 and 0.34 ± 0.01 from the spectrophotometric and conductometric methods, respectively, suggesting that these values of *K<sub>f</sub>* are very low. In the <sup>13</sup>C NMR, there is no direct measure of changes in aromatic carbon electron density between compound **1** and the ligand HB<sup>−</sup> which would enable a distinction between donor and acceptor functions of the aromatic ring to be made in the solution state. This point and also very low formation constant of the complex may say that interaction between ligand HB<sup>−</sup> and Tl<sup>I</sup> ions in the solution state is very weak and the polymeric complex in compound **1** cannot retain in solution state and probably as it anticipate extensive solvation occur in both methanol and DMSO.

In summary, the structure of compound **1** is novel and interesting because it represents a new, rarely observed two-dimensional framework self-assembled from polyhapto–aromatic interactions in thallium(I) coordination, and indicates the active lone pair on Tl<sup>I</sup> in this compound may be covered by involvement in donor bonding.

## Acknowledgement

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## Appendix A. Supplementary material

CCDC 628812 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving>.

html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.019.

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- [18] 4-Hydroxybenzoic acid (1 mmol, 0.138 g) was dissolved in 20 ml MeOH and was mixed and stirred with solution of 2 mmol (0.114 g) KOH in 3 ml H<sub>2</sub>O, then a solution of 2 mmol (0.533 g) TiNO<sub>3</sub> in 5 ml H<sub>2</sub>O was added to the mixture and was heated and stirred for an hour. After filtering it was allowed to evaporate for several days and then suitable colorless crystals were obtained. The crystals were washed with acetone and air dried, d.p. = 185 °C, Yield: 0.150 g (44%, based on H<sub>2</sub>B). C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>Ti: C, 24.59; H, 1.45; Ti, 59.82. Found: C, 24.80; H, 1.60; Ti, 59.10. IR (selected bands; in cm<sup>-1</sup>): 614 m, 777 m, 851 m, 1096 w, 1160 m, 1248 s, 1382 vs, 1522 vs, 1585 s. <sup>1</sup>H NMR (DMSO): 6.62–6.81 (d, 2H), 7.61–7.83 (d, 2H), 9.34–10.22 (broad, 1H) ppm. <sup>13</sup>C–{<sup>1</sup>H} NMR (DMSO): 114.42, 130.92, 132.15, 159.88 and 172.21 ppm.
- [19] Crystallographic measurements were made at 298(2) K using a Bruker APEX area-detector diffractometer. The intensity data were collected within the range  $3.17 \leq \theta \leq 24.83^\circ$  using graphite monochromated Mo-K $\alpha$  radiation for a crystal of dimension  $0.36 \times 0.20 \times 0.17$  mm. The structure was solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$ . The all H atoms were positioned geometrically and allowed to ride on their parent atoms. Structure solution and refinement was accomplished using SIR97, SHELXL97 and WINGX [G. Ferguson, C. Glidewell and E.S. Lavender, *Acta Crystallogr., Sect. B* 55 (1999) 591 and G.M. Sheldrick, SHELXTL-97 V5.10, 1997, Bruker AXS Inc., Madison, WI-53719, USA]. Plots were prepared with ORTEP III [L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.] and Mercury [Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, 2001–2005]. Crystal data: formula, C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>Ti;  $M_r$  341.48 g/mol; orthorhombic system, space group *Pbca*;  $a = 10.7085(13)$ ,  $b = 10.3621(13)$ ,  $c = 12.7184(16)$  Å,  $V = 1411.3(3)$  Å<sup>3</sup>;  $D_c = 3.214$  Mg/m<sup>3</sup> ( $Z = 8$ );  $F(000) = 1216$ ;  $R(wR) = 0.0224$  (0.0544) for 1245 reflections, with  $I > 2\sigma(I)$ ;  $R(wR) = 0.0279$  (0.0564) for all data.
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