

Thallium(I) Salicylate and Phthalate: Syntheses and Structural Characterization

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Two new 2D polymers, thallium(I) hydrogensalicylate (**1**) and hydrogenphthalate (**2**), have been synthesized and characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy. The single-crystal X-ray data show the coordination number of the Tl^I ions of compounds **1** and **2** to be four and six with the environment TlO₄ and TlO₆, respectively. The arrangement of the O atoms suggests a gap in the coordination geometry around the thallium atoms in both compounds, due to a stereo-chemically 'active' electron lone pair of Tl^I. There is another interaction between the thallium atom and the carbon atoms of an aromatic ring in compound **1**, giving a total hapticity of ten with the environment C₆O₄Tl.

Key words: Thallium, Crystal Structure, Lone Pair, Phthalate, Salicylate

Introduction

Thallium reagents, despite their inherent toxicity and cost, have played an important role in the development of modern inorganic and organometallic chemistry [1–10]. Thallium, when compared with the remainder of the group 13 elements, shows a preference for the oxidation state +1. This has been attributed to the effect of the inert pair of electrons introduced by Sidgwick and generally used in introductory textbooks to explain the tendency of the heavier main-group elements to adopt oxidation numbers that are 2 less than the respective group number. This phenomenon originates from a combination of shell structure effects and relativity. Owing to the relativistic downshift in energy of the 6s orbital, Tl does indeed favor the oxidation state +1 over +3. Moreover, Tl might be regarded as a relativistic alkali metal because Tl chemistry parallels that of the alkali metals in many ways [7].

In recent works we have reported the crystal structures of a Tl^I phthalate [2–3], and in this paper we extend this subject to include hydrogensalicylate and –phthalate which are found to be two-dimensional polymers with a stereo-chemical activity of the Tl(I) valence shell electron lone pair.

Results and Discussion

The reaction between thallium(I) nitrate and mixtures of sodium salicylate/phthalate in methanol

gives the crystalline materials {Tl[(H)salicylate)]}_n (**1**)/{Tl[(H)phthalate)]}_n (**2**). The IR spectra of these compounds show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1523 cm⁻¹ range. The relatively weak bands at around 3040 and 3050 cm⁻¹ are assigned to the ν(CH) mode of the salicylate and phthalate rings in **1** and **2**, respectively. The broad absorption band for ν(H-O) appears at *ca.* 3420 and 3430 cm⁻¹, respectively, attributable to ν(O-H...X) hydrogen bonds. The structures of compounds **1** and **2** were confirmed by X-ray crystallography.

Determination of the structure of the **1** and **2** by X-ray diffraction (Table 1, Figs 1 and 2) has shown the compounds to be two-dimensional polymers (Figs 3 and 4). The thallium atoms can be considered to be four- and six-coordinate, respectively. The separations between the thallium atoms are 4.33(2) and 4.037(3) Å in **1** and **2**, respectively, longer than the sum of van der Waals radii of *ca.* 3.92 Å [10] of two Tl^I. Hence, a thalophilic Tl...Tl interaction in these compounds can not be considered. The (H)salicylate⁻ anion acts as a tetradentate ligand, connecting four Tl^I ions. The carboxylate group of this ligand acts only as a bridging unit (Fig. 1). The carboxylate groups of the (H)phthalate⁻ ligand act as both bidentate chelating, and bridging units. Two oxygen atoms of one -COO group coordinate to a thallium(I) ion, also these oxy-

Identification code	1	2
Empirical formula	C ₇ H ₅ O ₃ Tl	C ₈ H ₅ O ₄ Tl
Formula weight	341.48	369.49
Temperature [K]	293(2)	120(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pbca</i>	<i>Pca2</i> ₁
Unit cell dimensions [Å]		
<i>a</i>	8.8021(18)	9.9915(8)
<i>b</i>	8.2930(19)	12.8729(11)
<i>c</i>	19.773(4)	6.5646(6)
Volume [Å ³]	1443.4(5)	844.34(13)
<i>Z</i>	8	4
Density (calculated) [g/cm ³]	3.14	2.91
Absorption coefficient [mm ⁻¹]	22.3	19.1
<i>F</i> (000)	1216	664
Crystal size [mm ³]	0.30 × 0.20 × 0.20	0.17 × 0.17 × 0.25
θ Range for data collection [°]	2.06 to 30.06	2.58 to 27.49
Index ranges	0 ≤ <i>h</i> ≤ 12 0 ≤ <i>k</i> ≤ 11 −27 ≤ <i>l</i> ≤ 27	−7 ≤ <i>h</i> ≤ 12 −6 ≤ <i>k</i> ≤ 16 −8 ≤ <i>l</i> ≤ 8
Reflections collected	3891	6439
Independent reflections	2072 [<i>R</i> (int) = 0.0454]	1755 [<i>R</i> (int) = 0.0267]
Completeness to theta [%]	98.0	96.8
Max. and min. transmission	0.034 and 0.004	0.022 and 0.014
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2072/0/100	1755/1/121
Goodness-of-fit on <i>F</i> ²	0.938	1.089
Final <i>R</i> Indicate [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0367, <i>wR</i> 2 = 0.0744	<i>R</i> 1 = 0.0376, <i>wR</i> 2 = 0.0860
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0679, <i>wR</i> 2 = 0.0788	<i>R</i> 1 = 0.0421, <i>wR</i> 2 = 0.0876
Largest diff. Peak and hole [e·Å ⁻³]	1.85 and −1.14	1.97 and −2.00
Flack's parameter		−0.00(2)

Table 1. Crystal data and structure refinement for [Tl((H)salicylate)]_n (**1**) and {Tl[(H)phthalate]}_n (**2**).

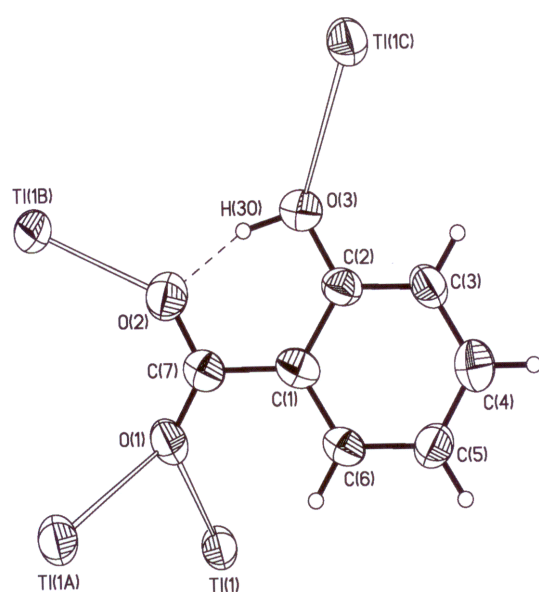


Fig. 1. ORTEP diagram of the asymmetric unit of [Tl((H)salicylate)]_n (**1**), showing intramolecular hydrogen bonding.

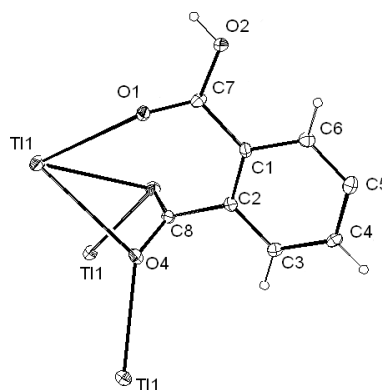
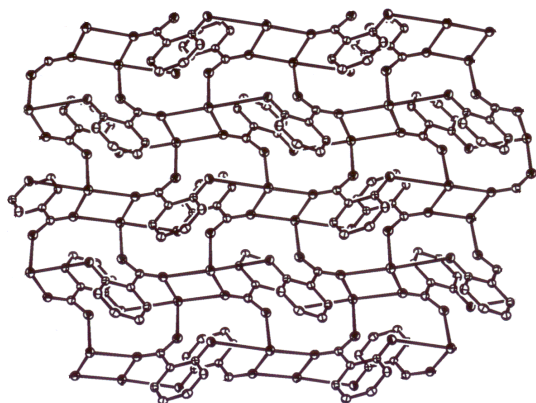
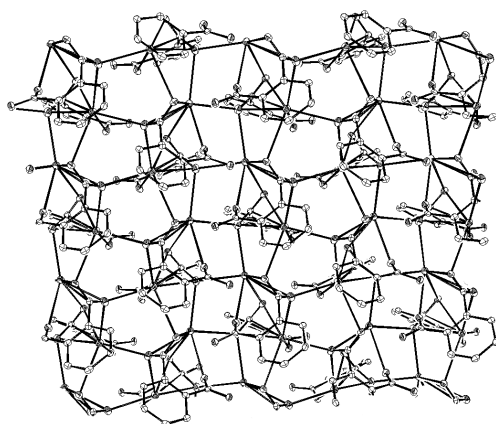


Fig. 2. ORTEP diagram of the asymmetric unit of {Tl[(H)phthalate]}_n (**2**).

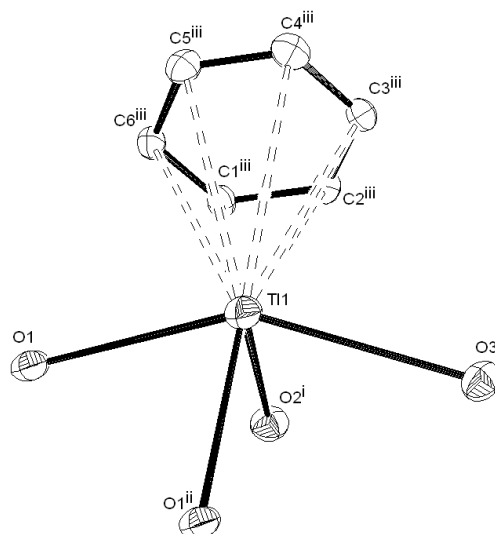
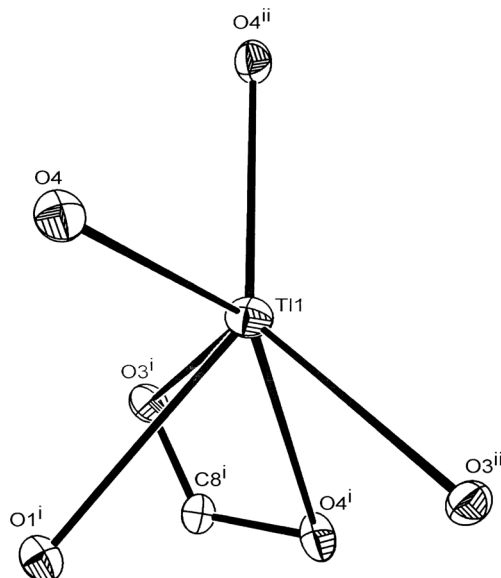
gen atoms bridge to four other thallium atoms. Interestingly, one of the oxygen atoms in this compound is linked to three different thallium atoms, a very novel and interesting behavior of carboxylate groups (Fig. 4). The oxygen atom of the –OH group is coordinated to thallium atoms in **1** whereas this group in the **2** is not coordinated to thallium atoms.

The arrangement of the oxygen atoms of the (H)salicylate[−] and (H)phthalate[−] ligands suggest a gap in the coordination geometry around the metal ions

Fig. 3. 2D frame of the $[\text{Tl}((\text{H})\text{salicylate})]_n$ (**1**).Fig. 4. 2D frame of the $\{\text{Tl}[(\text{H})\text{phthalate}]\}_n$ (**2**).

in the both compounds, occupied possibly by a stereo-active lone pair of electrons on the thallium atoms. The observed shortening of the Tl-O bonds on the side of Tl ion opposite to the putative lone pair ($\text{Tl1-O2}^{\text{i}} = 2.54(6)$ and $\text{Tl1-O4} = 2.743(8)$ Å compared with $\text{Tl1-O3} = 2.93(5)$ and $\text{Tl1-O4}^{\text{ii}} = 3.035(9)$ Å adjacent to the lone pair in **1** and **2**, respectively) (Figs 5 and 6) supports the presence of this feature [12].

With a low formal coordination number of 4 for the Tl atom in **1**, one tends to look for secondary interactions that could possibly relieve this coordinative unsaturation. To find other potential donor centers, it is necessary to extend the bonding limit. A search was made generally for $\text{Tl}\cdots\text{C}$ approaches in **1** and **2**, and it appears that the Tl atoms of **1** may also be involved in an η^6 interaction with the phenyl groups of salicylate anion. The Tl^{I} atom in **1** has contacts to six carbon atoms of a phenyl ring, with distances $\text{C1}^{\text{iii}}\cdots\text{Tl} = 3.91(5)$, $\text{C2}^{\text{iii}}\cdots\text{Tl} =$

Fig. 5. Environment of the Tl-atom in $[\text{Tl}((\text{H})\text{salicylate})]_n$ (**1**), showing of $\text{Tl}\cdots\text{C}$ interactions on extending the bonding limit.Fig. 6. Environment of the Tl-atoms in $\{\text{Tl}[(\text{H})\text{phthalate}]\}_n$ (**2**).

$3.90(4)$, $\text{C3}^{\text{iii}}\cdots\text{Tl} = 3.81(4)$, $\text{C4}^{\text{iii}}\cdots\text{Tl} = 3.72(4)$, $\text{C5}^{\text{iii}}\cdots\text{Tl} = 3.69(6)$ and $\text{C6}^{\text{iii}}\cdots\text{Tl} = 3.79(4)$ Å (Fig. 5). Hence, its coordination sphere in **1** is completed to obtain an irregular ten coordination. The reported $\text{Tl}\cdots\text{C}$ separations range is 3.20–4.00 Å in recently reported species [5, 13]. Thus, hexahapto aromatic coordination of Tl(I) appears to be yet another factor which can make varying contributions to the sta-

bility of complexes of this metal ion. A recent report of polyhapto-aromatic interactions in lead(II) coordination has suggested that the active lone pair of Pb(II) may be involved in donor bonding [14]. A comparison to the usual results may indicate that the unusually high coordination number in **1** reflects the capacity of Tl(I) to act like Pb(II) as both a Lewis acid and a Lewis base.

Experimental Section

Sample characterization

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. The ^1H and ^{13}C NMR solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

Preparation of $\{[\text{Tl}(\text{H})\text{salicylate}]\}_n$ (**1**)

The compound was prepared by dissolving 0.266 g (1 mmol) of thallium(I) nitrate in distilled water and methanol and adding a mixture of phthalic acid (0.158 g, 1 mmol) and sodium hydroxide (0.04 g, 1 mmol) in methanol. The resulting mixture was stirred for 1 h. The solution was allowed to stand at room temperature for several days. After evaporation of the solvent crystals were obtained (m.p. > 300 °C). Yield: 0.170 g, 50%. $\text{C}_7\text{H}_5\text{O}_3\text{Tl}$: C 24.59; H 1.45; Tl 59.82; found: C 24.80; H 1.60; Tl 59.10. – IR (cm^{-1}) selected bonds: ν = 662(m), 754(s), 801(m), 850(m), 1023(w), 1134(s), 1292(vs), 1318(vs), 1382(vs), 1473(vs), 1580(vs), 2645(w), 3040(w), and 3420(m). – ^1H NMR ($[\text{D}_6]$ -DMSO): δ = 7.6 (t, 2H), 8.1(t, 2H), and 12.7(b, 1H) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]$ -DMSO): δ = 116.4, 117.1, 121.1, 130.4, 132.4, 162.4, 173.2 ppm.

Preparation of $\{[\text{Tl}(\text{H})\text{phthalate}]\}_n$ (**2**)

The compound was prepared by dissolving 0.266 g (1 mmol) of thallium(I) nitrate in distilled water and methanol and adding a mixture of phthalic acid (0.186 g, 1 mmol) and sodium hydroxide (0.04 g, 1 mmol) in methanol. The resulting solution was stirred and then allowed to stand for several days at room temperature. Slow evaporation of the solvent at room temperature yielded crystals suitable for X-ray analysis. The crystals were washed with acetone and air dried (m.p. = 272 °C). Yield: 0.166 g, 45%. $\text{C}_8\text{H}_5\text{O}_4\text{Tl}$: calcd: C 25.98; H 1.35; Tl 55.11; found: C 25.82; H 1.50; Tl 54.10. – IR (cm^{-1}) selected bonds: ν = 667(m), 751(s), 799(s), 1071(m), 1141(s), 1270(vs), 1300(vs), 1470(vs), 1520(vs), 1650(m), 2885(w), 3050(w), and 3430(m). – ^1H NMR ($[\text{D}_6]$ -DMSO): δ = 7.5 (t, 2H),

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Tl}(\text{H})\text{salicylate}]_n$ (**1**).

Tl1-O2 ⁱ	2.54(6)	Tl1-O1 ⁱⁱ	2.62(6)
Tl1-O1	2.81(6)	Tl1-O3	2.92(5)
Tl1 ⁱ -Tl1 ⁱⁱⁱ	4.33(2)		
C1 ⁱⁱⁱ -Tl1	3.91(5)	C2 ⁱⁱⁱ -Tl1	3.90(4)
C3 ⁱⁱⁱ -Tl1	3.81(4)	C4 ⁱⁱⁱ -Tl1	3.72(4)
C5 ⁱⁱⁱ -Tl1	3.69(6)	C6 ⁱⁱⁱ -Tl1	3.79(4)
Tl1-O2 ⁱ -Tl1-O1 ⁱⁱ	79.5(2)	O2 ⁱ -Tl1-O1	74.7(2)
O1 ⁱⁱ -Tl1-O1	74.2(2)	O2 ⁱ -Tl1-O3 ⁱⁱⁱ	84.1(2)
O1 ⁱⁱ -Tl1-O3 ⁱⁱⁱ	81.7(2)	O1-Tl1-O3 ⁱⁱⁱ	150.3(2)

Symmetry codes: ⁱ: $x + 1/2, -y + 1/2, -z + 1$, ⁱⁱ: $-x + 1, -y, -z + 1$, ⁱⁱⁱ: $x + 1, y, z$.

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for $\{[\text{Tl}(\text{H})\text{phthalate}]\}_n$ (**2**).

Tl1-O4	2.74(8)	Tl1-O4 ⁱⁱ	2.83(9)
Tl1-O3 ⁱ	2.88(8)	Tl1-O1 ⁱ	2.96(8)
Tl1-O3 ⁱⁱⁱ	2.98(8)	Tl1-O4 ⁱ	3.03(9)
O4-Tl1-O4 ⁱⁱ	91.3(2)	O4-Tl1-O3 ⁱ	123.6(2)
O4 ⁱⁱ -Tl1-O3 ⁱ	85.8(2)	O4-Tl1-O1 ⁱ	81.3(2)
O4 ⁱⁱ -Tl1-O1 ⁱ	136.1(2)	O3-Tl1-O1 ⁱ	64.0(2)
O4-Tl1-O3 ⁱⁱⁱ	96.2(3)	O4 ⁱⁱ -Tl1-O3 ⁱⁱⁱ	136.0(2)
O3 ⁱ -Tl1-O3 ⁱⁱⁱ	123.60(19)	O1 ⁱ -Tl1-O3 ⁱⁱⁱ	87.9(2)
O4-Tl1-O4 ⁱ	147.7(3)	O4 ⁱⁱ -Tl1-O4 ⁱ	113.5(3)
O3 ⁱ -Tl1-O4 ⁱ	44.1(2)	O1 ⁱ -Tl1-O4 ⁱ	66.6(2)
O3 ⁱⁱⁱ -Tl1-O4 ⁱ	80.5(2)		

Symmetry codes: ⁱ: $x - 1/2, -y + 1, z$, ⁱⁱ: $-x + 1/2, y, z + 1/2$, ⁱⁱⁱ: $-x + 1/2, y, z - 1/2$.

8.1(t, 2H), and 12.5(b, 1H) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_6]$ -DMSO): δ = 130.2, 132.3, 135.0 and 168.1 ppm.

X-ray crystallography

X-ray measurements were made at 293(2) K and 120(2) K using a Siemens R3m/V diffractometer for compounds **1** and **2**, respectively. Accurate unit cell parameters and the orientation matrix for data collection were obtained from least-squares refinement. The structures have been solved by direct methods and refined by full-matrix least-squares on F^2 . The positions of hydrogen atoms were calculated at idealized geometrical positions and included in the structure-factor calculation as fixed-atom contributions. The absolute structure of **2** was determined by refinement of Flack's parameter $x = -0.00(2)$ [15].

Crystal data and refinement parameters are given in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

Supplementary material

Complete bond lengths and angles, co-ordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 283537 for **1** and 270820 for **2**.

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| [1] A. R. Mahjoub, A. Morsali, H. Bagherzadeh, <i>Polyhedron</i> 21 , 2555 (2002). | [8] H. Schumann, C. Janiak, J. Pickardt, U. Borner, <i>Angew. Chem., Int. Ed. Engl.</i> 26 , 789 (1987). |
| [2] M. R. Fadaei, A. Morsali, Ali R. Mahjoub, <i>Z. Naturforsch</i> 60b , 741 (2005). | [9] C. Janiak, R. Hofmann, <i>J. Am. Chem. Soc.</i> 112 , 5924 (1990). |
| [3] A. Askarinejad, A. Morsali, <i>J. Coord. Chem.</i> 59 , (2006), in press. | [10] C. Janiak, R. Hofmann. <i>Angew. Chem., Int. Ed. Engl.</i> 28 , 1688 (1989). |
| [4] M. Rafizadeh, V. Amani, B. Neumüller, <i>Z. Anorg. Allg. Chem.</i> 631 , 1753 (2005). | [11] F. Wiesbrock, H. Schmidbaur, <i>J. Am. Chem. Soc.</i> 125 , 3622 (2003). |
| [5] F. Wiesbrock, H. Schmidbaur, <i>J. Am. Chem. Soc.</i> 125 , 3622 (2003). | [12] R. D. Hancock, M. S. Shaikjee, S. M. Dobson, J. C. A. Boeyens, <i>Inorg. Chim. Acta</i> 154 , 229 (1988). |
| [6] H. M. Alvarez, P. A. Gillespie, D. Rabinovich, <i>Polyhedron</i> 23 , 617 (2004). | [13] J. Beck, J. Strähle, <i>Z. Naturforsch.</i> 41b , 1381 (1986). |
| [7] A. V. Mudring, F. Rieger, <i>Inorg. Chem.</i> 44 , 6240 (2005). | [14] J. M. Harrowfield, S. Maghaminia, A. A. Soudi, <i>Inorg. Chem.</i> 43 , 1810 (2004). |
| | [15] H. D. Flack, <i>Acta Crystallogr.</i> A39 , 876 (1983). |