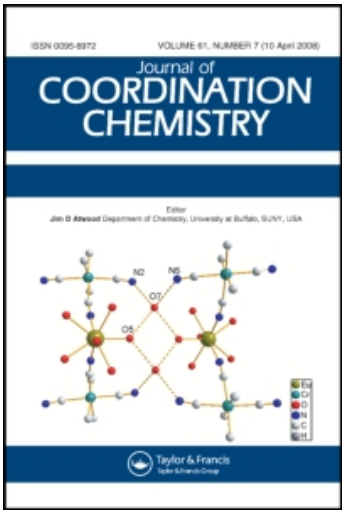

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structural characterization of a new two-dimensional polymeric thallium(I) compound, {Tl[(H)phthalate)]}n

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To cite this Article Askarinejad, Azadeh and Morsali, Ali(2006) 'Synthesis and structural characterization of a new two-dimensional polymeric thallium(I) compound, {Tl[(H)phthalate)]}n', Journal of Coordination Chemistry, 59: 9, 997 — 1005
To link to this Article: DOI: 10.1080/00958970500448226
URL: http://dx.doi.org/10.1080/00958970500448226

Journal of Coordination Chemistry
Vol. 59, No. 9, 15 June 2006, 997–1005

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Synthesis and structural characterization of a new two-dimensional polymeric thallium(I) compound, $\{Tl[(H)phthalate)]\}_n$

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(*Received 3 May 2005; in final form 3 August 2005*)

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A two-dimensional polymer, $\{Tl[(H)phthalate)]\}_n$, has been synthesized and characterized by elemental analysis, IR-, ^1H NMR- and ^{13}C NMR spectroscopy. The single-crystal X-ray data show the coordination number Tl^I ion is six, TlO_6. However, the arrangement of O-atoms suggests a gap or hole in the coordination geometry around thallium. A stereo chemically 'active' electron lone pair of Tl^I possibly occupies this 'hole'.

Keywords: Thallium; Crystal structure; Lone pair; Phthalate ligand

1. Introduction

Thallium reagents, despite their inherent toxicity and cost, have played a conspicuous role in the development of modern inorganic and organometallic chemistry [1, 2]. Thallium(I) compounds are interesting because of unique characteristics such as the potential ability to form metal–metal bonds or metal–carbon bonds, presence of high coordination number because of large size of thallium(I) ion, and the presence of a lone pair of electrons in the valence shell of Tl^I [3–7]. From a structural study of some Tl^I compounds [3], it has been argued that the ''stereochemical activity'' plays an important role in determining the solid-state geometry of these compounds [7]. It was anticipated that this might be true for the Tl^I complex of the phthalate anion, which is an interesting ligand, with two carboxylate groups available for coordination (scheme 1).

Because of its ability for spontaneous aggregation of several ligand and metal ions this ligand may also be a very good candidate for investigation of the ''stereochemical activity'' of valence shell electron lone pairs in polymeric and supramolecular Tl^I compounds. In a recent study [8], we reported the the 2D structure

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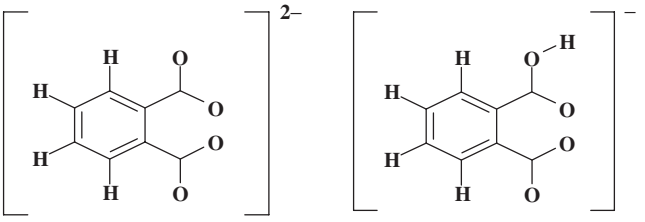
Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500448226



[phthalate^{2-}] [(H)phthalate^{-}]

Scheme 1. The formula structures of [phthalate^{2}] and [(H)phthalate^{-}].

of the 1 : 2 (phthalate : thallium) adduct, $[Tl_2(phthalate)]$. The present determination of the structure of the 1 : 1 adduct of thallium(I) with monobasic phthalate [(H)phthalate^{-}] anion, $\{Tl[(H)phthalate)]\}_n$ provides a novel two-dimensional polymer with "stereochemical activity" of valence shell electron lone pairs.

2. Experimental

2.1. *Physical measurements*

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 ^{1}H and ^{13}C NMR solution NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

2.2. *Preparation of [Tl((H)phthalate)]$_n$*

The compound $\{Tl[(H)phthalate)]\}_n$ was prepared by dissolving 0.266 g (1 mmol) 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 some days at room temperature. Slow evaporation of the solvent at room temperature yielded suitable crystals for X-ray analysis (m.p. = 272°C). The crystals were washed with acetone and air dried. IR (selected bands; in cm^{-1}): 667m, 751s, 799s, 1071m, 1141s, 1270vs, 1300vs, 1470vs, 1520vs, 1650m, 2885w, 3050w, 3430m. Anal. Calcd for $C_8H_5O_4Tl$: C 25.98, H 1.35, Tl 55.11; found: C 25.82, H 1.50, Tl 54.10. ^{1}H NMR (DMSO): $\delta = 7.50$ (t, 2H), 8.14 (t, 2H), 12.5 (b, 1H) ppm. ^{13}C-$\{^{1}H\}$ NMR (DMSO): $\delta = 130.23$, 132.37, 135.00 and 168.04 ppm.

2.3. *X-ray crystallography*

X-ray measurements were made at 120(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $2.58 \leq \theta \leq 27.49°$ using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The intensities of 6439 unique reflections were collected, from which 1525 with

Table 1. Crystal data and structure refinement for $\{Tl[(H)phthalate)]\}_n$.

Empirical formula	$C_8H_5O_4Tl$
Formula weight	369.49
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions (Å)	$a = 9.9915(8)$ $b = 12.8729(11)$ $c = 6.5646(6)$
Volume (Å^3)	844.34(13)
Z	4
Density (calculated) (g cm^{-3})	2.907
Absorption coefficient (mm^{-1})	19.104
$F(000)$	664
Crystal size (mm^3)	$0.35 \times 0.20 \times 0.20$
Theta range for data collection (°)	2.58 to 27.49
Index ranges	$-7 \le h \le 12$, $-6 \le k \le 16$, $-8 \le l \le 8$
Reflections collected	6439
Independent reflections	1755 [R(int) = 0.0267]
Completeness to $\theta = 27.49$	96.8%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.022 and 0.014
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1755/1/121
Goodness-of-fit on F^2	1.089
Final R indices for 1525 ref1. [$I > 2\sigma(I)$]	$R_1 = 0.0376$, $wR_2 = 0.0860$
R indices (all data)	$R_1 = 0.0421$, $wR_2 = 0.0876$
Absolute structure parameter	0.00(2)
Largest diff. peak, hole (e Å^{-3})	1.965, −1.995

$I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. The positions of hydrogen atoms were calculated at idealized geometrical position and included in the structure-factor calculation as fixed-atom contributions. Corrections for Lorentz and polarization effects as well as a semi-empirical absorption correction were applied. All calculations were carried out with a PDP–11/23+ computer using the SDP-PLUS program package [9, 10].

Crystal data and refinement parameters are given in table 1. Selected bond lengths and angles are given in table 2. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in figures 1(a) and 3, respectively.

3. Results and discussion

3.1. *Syntheses*

Reaction between thallium(I) nitrate and mixtures of phthalic acid and sodium hydroxide in methanol provided the crystalline material $\{Tl[(H)phthalate)]\}_n$. The IR spectrum of this compound shows absorption bands resulting from skeletal vibrations of aromatic rings in the 1400–1523 cm^{-1} range. The relatively weak band at around 3050 cm^{-1} is assigned to the ν(CH) mode of phthalate aromatic rings.

Table 2. Selected bond lengths [Å] and bond angles [°] for $\{Tl[(H)phthalate)]\}_n$

Tl1-O4	2.743(8)
Tl1–O4^{ii}	2.833(9)
Tl1–O3^{i}	2.878(8)
Tl1–O1^{i}	2.961(8)
Tl1–O3^{iii}	2.980(8)
Tl1–O4^{i}	3.035(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)
O3T/1–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–T/–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: $-x+1/2, y, z-1/2$.

The broad absorption band for ν(H–O) is at ca 3430 cm^{-1}. The broad band is perhaps attributable to ν(O–H $\cdots$ X), indicating the presence of hydrogen bonds in this compound, which is confirmed by the crystal structure. The ^{1}H NMR spectrum of the DMSO solution of the compound displays two distinct rersonances at 7.50 (t, 2H) and 8.14 (t, 2H) ppm that have been assigned to the aromatic protons (Ha, and Hb (scheme 2), respectively) and one other broad resonance at 12.5 (b, 1H) ppm that has been assigned to –OH protons, Hc (scheme 2). The ^{13}C NMR spectrum of the DMSO solution of the complex displays four distinct absorption bands at 130.23, 132.37, 135.00 and 168.04 ppm assigned to the aromatic and carboxilate carbons, respectively. The structure of $\{Tl[(H)phthalate)]\}_n$ was confirmed by X-ray crystallography.

3.2. *Crystal structure of* $\{Tl[(H)phthalate)]\}_n$

Determination of the structure of the $\{Tl[(H)phthalate)]\}_n$ by X-ray crystallography (table 1) showed the compound to be a novel two-dimensional polymer (figure 1b). The thallium atoms can be considered six-coordinate (figure 2 and table 2) with separation between the thallium atoms of 4.037(3) Å, longer than the sum [7] of van der Waals radii of ca 3.92 Å [7]. Hence, a direct Tl–Tl interaction in this compound cannot be considered. Each "Hphthalate$^-$" anion acts as a hexadentate ligand, connecting four Tl^I ions. The carboxylate groups of the "Hphthalate$^-$" ligand act as both bidentate chelating, and bridging as two oxygen atoms of the carboxylate group coordinate to a thallium(I) and also two of these oxygen atoms bridge to four other thallium atoms. One oxygen in this compound is linked to three different thallium atoms, a very novel and interesting behavior of carboxylate groups (scheme 3 and figure 1b). The oxygen atom of the –OH group is not coordinated to thallium atoms.

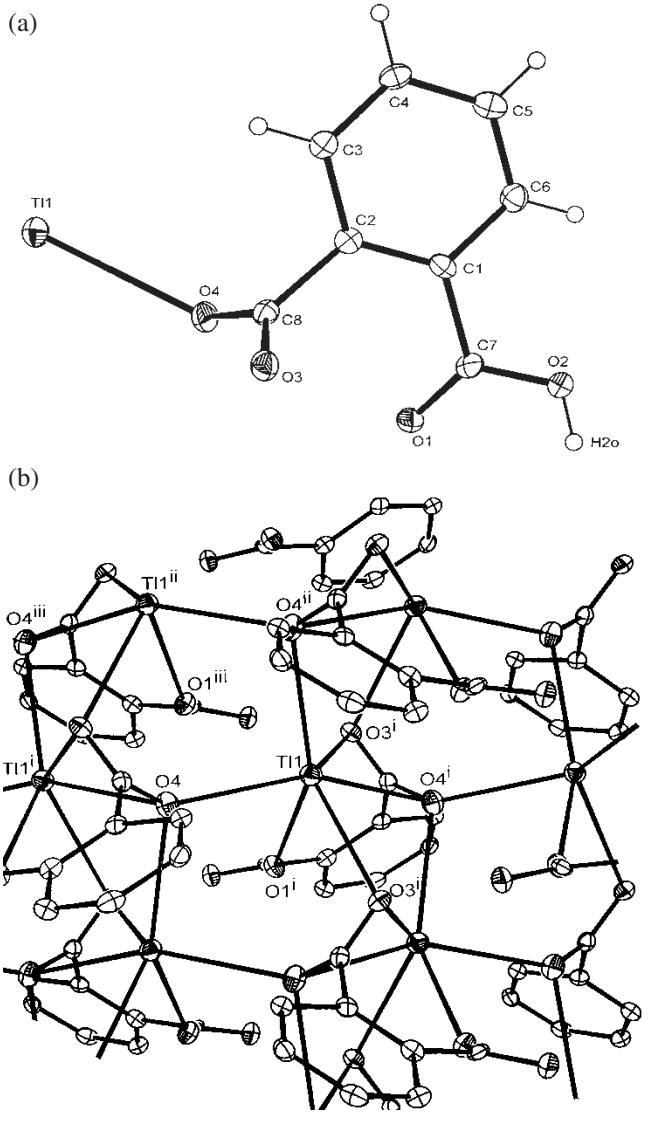
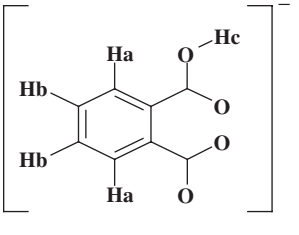


Figure 1. (a) ORTEP diagram of $\{Tl[(H)phthalate)]\}_n$ complex and (b) 2D-frame of the $\{Tl[(H)phthalate)]\}_n$ complex.



Scheme 2. Showing the three different hydrogen atoms in the structure of [(H)phthalate$^-$].

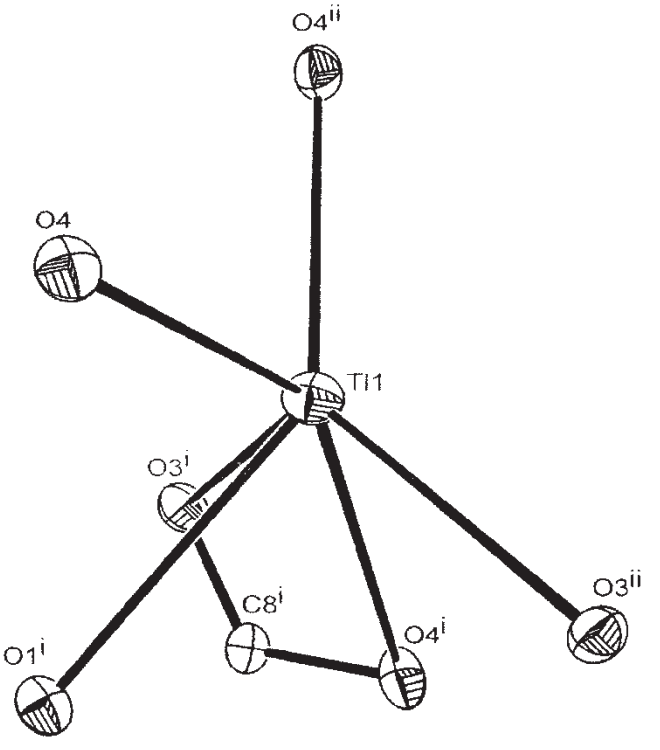
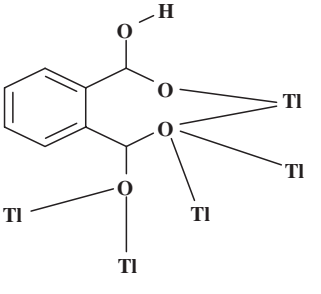


Figure 2. Environment of Tl-atoms in $\{Tl[(H)phthalate)]\}_n$ complex.



Scheme 3. The coordination mode of [(H)phthalate$^-$] ligand.

The arrangement of the oxygen atoms of the phthalate ligands suggest a gap or hole in the coordination geometry around the thallium, occupied possibly by a stereo-active lone pair of electrons. The observed shortening of the Tl–O bond on opposite to the putative lone pair (Tl1–O4 = 2.743(8) compared with Tl1–O4^{ii} = 3.035(9) Å adjacent to the lone pair) supports the presence of this feature [11].

The compound is linked by intermolecular hydrogen bonding (figure 3 and table 3). The uncoordinated –OH group of the "[(H)phthalate$^-$]" is involved in hydrogen bonding acting as hydrogen-bond acceptors with O atoms from adjacent "[(H)phthalate$^-$]" as potential hydrogen-bond donors.

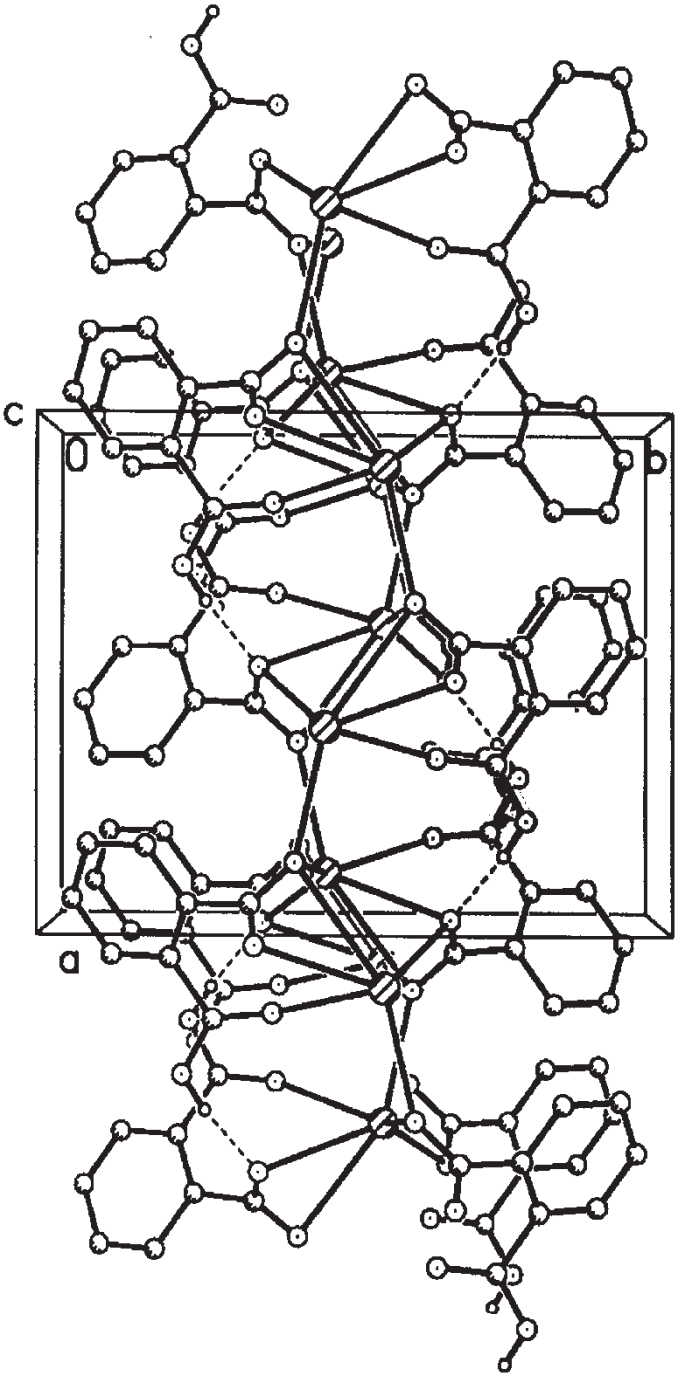


Figure 3. Unit cell of the $\{Tl[(H)phthalate)]\}_n$ complex, showing edge-to-edge π–π stacking interactions and hydrogen bonding.

Table 3. Intermolecular H-bonds in structure of the $\{Tl[(H)phthalate)]\}_n$ compound.

D–H···A	D···A (Å)	D–H (Å)	H···A (Å)	DHA (°)
O2–H2O···O3 ($-x+3/2$, y, $z-1/2$)	2.558(l2)	0.845	1.75	160

A π–π stacking [12, 13] interaction between the parallel aromatic rings belonging to adjacent chains in the complex exists as shown in figure 3. The phenyl groups are almost parallel and separated by a distance of about 3.5 Å, close to that of the layers in graphite. Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "edge-to-edge" types [14, 15]. The edge-to-edge interplanar distances are 3.678 Å, normal for π–π stacking [14, 15].

The striking similar feature of the $\{Tl[(H)phthalate)]\}_n$ compound with $[Tl((H)phthalate)]_n$ complex is that, there is π–π stacking interaction between the parallel aromatic rings belong to adjacent chain in both compounds. The π–π stacking in the $\{Tl[(H)phthalate)]\}_n$ is face-to-face type and in the $\{Tl[(H)phthalate)]\}_n$ is edge-to-edge type. The other similar feature of the $[Tl_2(phthalate)]_n$ complex with $\{Tl[(H)phthalate)]\}_n$ compound is that the lone pair in both compounds is stereo-chemically active.

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 270820 for $\{Tl[(H)phthalate)]\}_n$.

Acknowledgements

Support of this investigation by Tarbiat Modarres University is gratefully acknowledged.

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