Synthesis and Structural Characterization of a New Two-Dimensional Polymeric Thallium(I) Complex, $[Tl_2(phthalate)]_n$

M. R. Fadaei, A. Morsali, and Ali R. Mahjoub

Department of Chemistry, School of Science, Tarbiat Modarres University,
P. O. Box 14155-4838 Tehran. Iran

Reprint requests to Dr. A. Morsali or Dr. A. R. Mahjoub. Fax: +98 21 8006544.
E-mail: morsali_a@yahoo.com or almahjoub@yahoo.de

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Determination of the structure of the $[Tl_2(phthalate)]$ by X-ray crystallography shows that there are six (TlO_6) and five (TlO_5) coordinate Tl atoms. The complex is a two-dimensional coordination polymer.

Key words: Thallium, Crystal Structure, Lone Pair of Electron, Phthalate Ligand

Introduction

Thallium(I) complexes are interesting because of the in unique characteristics such as the potential ability to form metal-metal bonds and the presence of a lone pair of electron in the valence shell of the Tl^+ cation [1 – 2]. An issue frequently discussed in considering the coordination and stereo-active of heavy metals is that of the "stereo-chemical activity" of this lone pair. From a structural study some of Pb(II) complexes [3], it has been argued that this "stereo-chemical activity" plays an important role in determining the solid state geometry of these compounds. It was anticipated that this might be true for the Tl(I) complex of the phthalate anion. The present provides further support for this view in the thallium(I) compounds.

Experimental Section

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.

Preparation of [Tl_2(phthalate)]

The complex $[Tl_2(phthalate)]$ was prepared by dissolving 0.266 g (1 mmol) thallium(I) nitrate in distilled water and adding a mixture of phthalic acid (0.083 g, 0.5 mmol) and potassium hydroxide (0.057 g, 1 mmol) in ethanol (10 ml). The resulting solution was stirred for 1 h at room temperature, then it was allowed to stand for 2 – 3 d in a refrigerator. White crystals of the product precipitated, which were

Table 1. Crystal data and structure refinement for $[Tl_2(phthalate)]_n$.

Empirical formula	$C_8\ H_4\ 0_4\ Tl_2$
Formula weight	572.85
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 7.2963(14)$ Å
	$b = 6.1790(11)$ Å
	$c = 10.570(11)$ Å
	$\beta = 99.942(4)^\circ$
Volume	469.40(15) Å^3
Z	2
Density (calculated)	4.053 g/cm^3
Absorption coefficient	34.2 mm^{-1}
$F(000)$	492
Crystal size	$0.20 \times 0.10 \times 0.08$ mm^3
Theta range for data collection	2.83 to 30.08°
Index ranges	$-10 \le h \le 10$, $-8 \le k \le 8$,
	$-14 \le l \le 14$
Reflections collected	5574
Independent reflections	2657 [R(int) = 0.0594]
Completeness to $\theta = 30.060$	98.9%
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	0.80 and 0.27
Refinement method	full-matrix least-squares on F^2
Data / restraints / parameters	2657/1/129
Goodness-of-fit on F^2	0.908
Final R indices for	
2463 ref1. [$I > 2\sigma(I)$]	$R1 = 0.0405$, $wR2 = 0.1019$
R indices (all data)	$R1 = 0.0429$, $wR2 = 0.1035$
Absolute structure parameter	0.03(3)
Largest diff. peak, hole	2.848, -1.845 e·Å^{-3}

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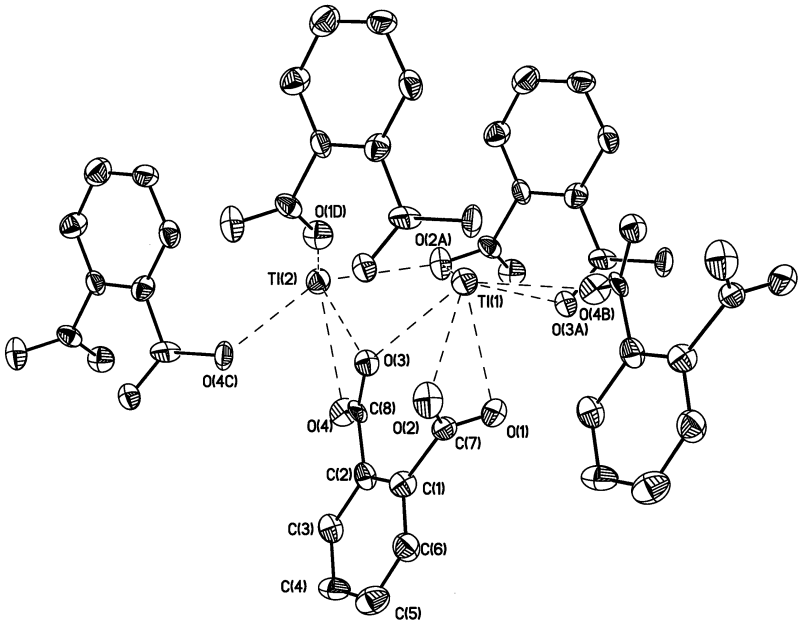

Fig. 1. ORTEP diagram a view of the Tl_2O_2 rhomb forming the basic link of the repeating polymeric units of $[Tl_2(phthalate)]_n$.

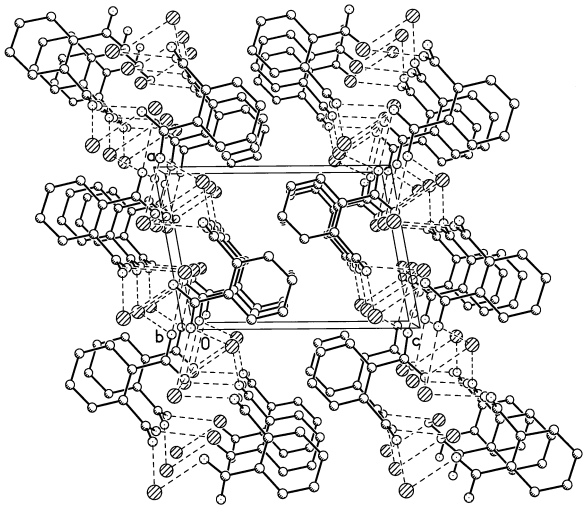

Fig. 2. The unit cell and showing π-π stacking interaction between phthalate ligands in $[Tl_2(phthalate)]_n$.

filtered off, washed with acetone and ether, and dried in air (0.4 g, yield 70%), m.p. 220 °C. Analysis for $C_8H_4O_4Tl_2$: calcd. C 16.75, H 0.70; found: C 16.60, H 0.79. IR(cm^{-1}) selected bands: υ = 754(w), 1392(s), 1554(vs), 3100(w). ^{1}H NMR (DMSO): δ = 8.25(m) ppm. ^{13}C-{^{1}H} NMR (DMSO): δ = 129.00, 131.10, 133.20, 170.00 ppm.

X-ray crystallography

X-ray measurements were made at 120(2) K using a Siemens R3 m/V diffractometer. The intensity data were collected within the range $2.83 \leq \theta \leq 30.08^\circ$ using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 5574 unique reflections were measured, 2657 of which were unique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2.

Table 2. Selected bond lengths [Å] and angles [°] for $[Tl_2(phthalate)]_n$.

Tl(1)-O(1)	2.777(9)	Tl(1)-O(3)$^{\#1}$	2.780(8)
Tl(1)-O(3)	2.895(7)	Tl(1)-O(2)$^{\#1}$	2.919(9)
Tl(1)-O(4)$^{\#1}$	2.931(8)	Tl(1)-O(2)	2.937(10)
Tl(2)-O(3)	2.509(8)	Tl(2)-O(2)$^{\#1}$	2.726(9)
Tl(2)-O(4)$^{\#3}$	2.823(8)	Tl(2)-O(1)$^{\#4}$	2.852(9)
Tl(1)-Tl(2)$^{\#2}$	3.8572(8)	Tl(1)-Tl(1)$^{\#3}$	4.0420(7)
Tl(1)-Tl(1)$^{\#1}$	4.0420(7)	Tl(1)-Tl(2)	4.0525(9)
Tl(1)-Tl(2)$^{\#1}$	4.0990(8)	Tl(2)-O(4)	2.969(8)
O(1)-Tl(1)-O(3)	63.8(3)	O(3)$^{\#1}$-Tl(1)-O(3)	103.3(2)
0(2)O(1)-Tl(1)-O(2)$^{\#1}$	97.0(3)	O(3)$^{\#1}$-Tl(1)-O(2)$^{\#1}$	65.0(2)
O(3)-Tl(1)-O(2)$^{\#1}$	65.9(2)	O(1)-Tl(1)-O(4)$^{\#2}$	77.2(2)
O(3)$^{\#1}$-Tl(1)-O(4)$^{\#2}$	64.7(2)	O(3)-Tl(1)-O(4)$^{\#2}$	140.5(2)
O(2)$^{\#1}$-Tl(1)-O(4)$^{\#2}$	127.7(3)	O(1)-Tl(1)-O(2)	45.7(3)
O(3)$^{\#1}$-Tl(1)-O(2)	112.4(3)	O(3)-Tl(1)-O(2)	63.4(2)
O(2)$^{\#1}$-Tl(1)-O(2)	126.68(15)	O(4)$^{\#2}$-Tl(1)-O(2)	85.8(2)
O(3)-Tl(2)-O(2)$^{\#1}$	74.2(3)	O(3)-Tl(2)-O(4)$^{\#3}$	69.8(2)
O(2)$^{\#1}$-Tl(2)-O(4)$^{\#3}$	143.9(3)	O(3)-Tl(2)-O(1)$^{\#4}$	70.8(3)
O(2)$^{\#1}$-Tl(2)-O(1)$^{\#4}$	90.6(3)	O(4)$^{\#3}$-Tl(2)-O(1)$^{\#4}$	77.7(3)
O(3)-Tl(2)-O(4)	47.7(2)	O(2)$^{\#1}$-Tl(2)-O(4)	86.6(3)
O(4)$^{\#3}$-Tl(2)-O(4)	69.29(10)	O(1)$^{\#4}$-Tl(2)-O(4)	116.6(2)

Symmetry codes $^{\#1}$ $-x-3, y-1/2, -z$; $^{\#2}$ $x-1$, y, z; $^{\#3}$ $-x-2$, $y+1/2$, z; $^{\#4}$ $-x-3$, $y+1/2$, $-z$.

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 [4–5].

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 and 2.

Discussion

Determination of the structure of the [Tl_2 (phthalate)] by X-ray crystallography (Table 1) showed the complex to be a novel two-dimensional polymer (Fig. 2). There are six (TlO_6) and five (TlO_5) coordinate Tl atoms. The environment of two thallium atoms is different, six and five donors coordinate the Tl atoms. Thus, one of the thallium atoms can be considered to be six–coordinate with Tl1-O distances of Tl1-O1 = 2.777(9), Tl1-O3 $(-x-3,\ y-1/2,\ -z) = 2.780(8)$, Tl1-O3 = 2.895(7), Tl1-O2 $(-x-3,\ y-1/2,\ -z) = 2.919(9)$, Tl1-O4 $(-x-3,\ y-1/2,\ -z) = 2.931(8)$, Tl1-O2 = 2.937(10) Å. The other thallium atoms can be considered to be five-coordinate with Tl2-O distances of Tl2-O3 = 2.509(8), Tl2-O2 $(-x-3,\ y-1/2,\ -z) = 2.726(9)$, Tl2-O4 $(-x-2,\ y+1/2,\ z) = 2.823(8)$, Tl2-O1 $(-x-3,\ y+1/2,\ -z) = 2.852(9)$, Tl2-O4 = 2.969(8) Å (Table 2). The arrangement of the oxygen atoms of the phthalate ligands suggest a gap or hole in the coordination geometry around the metal ions, occupied possibly by a stereo-active lone pair of electrons on both thallium atoms (Tl1 and Tl2). The observed shortening of the Tl-O bond on the side of Tl(I) ion opposite to the putative lone pair (Tl1-O1 = 2.777(9) compared with Tl1-O2 = 2.937(10) and Tl2-O3 = 2.509(8) compared with Tl2-O4 = 2.969(8) Å adjacent to the lone pair) supports the presence of this feature [6].

There are some "weak" Tl···Tl bonds in the polymeric state and the exact distances are Tl1-Tl2 $(x-1,\ y,\ z) = 3.8572(8)$ Å, Tl1-Tl1 $(-x-2,\ y+1/2,\ z) = 4.0420(7)$ Å, Tl1-Tl1 $(-x-2,\ y+1/2,\ z) = 4.0420(7)$ Å, Tl1-Tl2 = 4.0525(9) Å and Tl1-Tl2$(-x-3,\ y-1/2,\ -z) = 4.0990(8)$ Å (Table 2).

In the reported complex here, there is a π-π stacking [7–8] interaction between the parallel aromatic rings of adjacent chains as shown in Figure 2. The mean molecular planes are close to parallel and separated by a distance of $\sim$ 3.5 Å, close to that of the planes in graphite.

Parallel arrays of the planes of the aromatic moieties indicate that these interactions are of the "π-stacting" type, rather than "edge-to-face" or "vertex-to-face" types [9–13]. In the structure reported here, the interplanar distance is 4.55 Å, slightly longer than the normal π-π stacking [12–13].

A simple model to describe the nature of π-π interactions has been developed by Hunter et al. [14]. This model predicts that face-to-face π-stacked interactions will be disfavored due to the dominance of π-π repulsion. However, in offset π-stacked, and edge-on or T-shaped geometries, favourable π-σ attractions dominate.

Thus two factors, lone pair activity and π-π stacking control the coordination sphere of this complex. The obvious question then is whether the lone pair activity has stretched coordinate bonds to result in ligand stacking or whether it is the stacking interaction, which has imposed a positioning of the donor atoms for forming gap in the coordination sphere. Since the model of face-to-face π-stacked interactions must be disfavored due to the dominance of π-π repulsion. This possibly suggests that lone pair activity may be the most important factor and affect on forming of π-π stacking.

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 227360 for $[Tl_2(\text{phthalate})]_n$.

Acknowledgement

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