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The Crystal Structure of Thallium(I) 1,2,4,5-Benzenetetracarboxylate

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Salts of 1,2,4,5-benzenetetracarboxylic acid (PMA) have a number of possible uses [1–3]. In order to better characterize the mode of coordination (if any) of the carboxylate group to the metal ion by IR and Raman spectroscopy, it is desirable to have single crystal X-ray crystal studies to serve as a basis for correlation of spectra and structure [4]. The structures of a copper, cobalt, uranyl, and two neptunium salts of PMA have been determined recently as well as the dihydrate of the acid which was done some time ago [1, 5–9]. The structures and vibrational spectra of the salts of PMA which have had their structure determined so far are greatly influenced by the extensive hydrogen bonding present. The thallium salt of PMA in this study is important as a standard for comparison because the structure and vibrational spectra are not influenced by hydrogen bonding or coordination of carboxylate groups to the metal ion. This has been very helpful in studying the vibrational spectra of other salts of PMA [10].

Crystal Data

$Tl_4C_{10}H_2O_8$, $M = 1067.61$, crystal size $0.13 \times 0.22 \times 0.52$ mm, monoclinic, $a = 7.374(3)$, $b = 6.212(2)$, $c = 14.945(5)$ Å, $\beta = 99.78(3)°$, $V = 674.6(4)$ Å^3 (by least-squares refinement of 15 diffractometer measured reflections), $D_m = 5.5$ g cm^{-3} (by displacement), $Z = 2$, $D_{calc} = 5.258$ g cm^{-3}, space group $P2_1/n$, Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator), $\mu = 48.2$ mm^{-1}. A computer-controlled four circle Nicolet autodiffractometer was used to collect 1550 reflections within the collection range $3.0° < 2\theta < 55°$, 1349 reflections $I > 3\sigma(I)$ were used for the refinement, $R = 0.057$, anomalous dispersion corrections were made for thallium, non-hydrogen atoms anisotropic, hydrogen atoms isotropic. Solved using heavy atom Patterson techniques using Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystalytics Co.

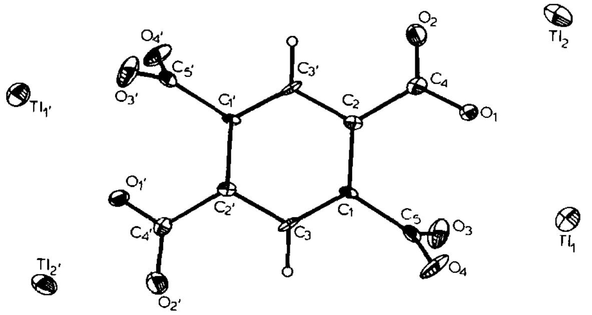

Fig. 1. A perspective drawing of $Tl_4[(O_2C)_4C_6H_2]$ with non-hydrogen atoms represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; the two hydrogen atoms are represented by arbitrarily-small spheres which are in no way representative of their true thermal motion. Atoms labeled with a prime (′) are related to those without a prime by the crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the unit cell.

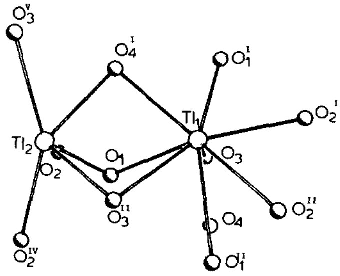

Fig. 2. A perspective drawing of the 1st coordination sphere for the two independent Tl atoms in crystalline $Tl_4[(O_2C)_4C_6H_2]$. All atoms are represented by arbitrary-sized spheres for purposes of clarity. Atoms labeled with a superscripted Roman numeral are related to those without superscripts by the following symmetry operations: I, $1\frac{1}{2} - x$, $-\frac{1}{2} + y$. $\frac{1}{2} - z$; II, $1\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; III, $1 + x, y, z$; IV, $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; V, $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$.

A perspective view of the compound is shown in Fig. 1. Figure 2 is a perspective drawing of the first coordination spheres for the two independent thallium atoms. Bond distances and principal bond angles are given in Table I.

One of the two crystallographically-independent thallium ions is surrounded by nine carboxylate oxygens at distances of 2.79(1) to 3.51(1) Å in a distorted tricapped trigonal prism; the second thallium ion is surrounded by six carboxylate oxygens at distances of 2.51(1) to 3.51(1) Å. These distances indicate predominantly ionic interactions

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TABLE I. Principal Bond Lengths (Å) and Angles (°) in $Tl_4C_{10}H_2O_8$

Type^{a-d}	Length (Å)	Type^{a-d}	Length (Å)
$Tl_1\cdots O_1$	2.94(1)	$Tl_2\cdots O_1$	2.53(1)
$Tl_1\cdots O_3$	2.79(1)	$Tl_2\cdots O_2$	3.05(1)
$Tl_1\cdots O_4$	2.95(1)	$Tl_2\cdots O_3^{II}$	2.81(1)
$Tl_1\cdots O_2^{III}$	2.97(1)	$Tl_2\cdots O_4^{I}$	2.79(1)
$Tl_1\cdots O_3^{II}$	3.15(1)	$Tl_2\cdots O_2^{IV}$	3.01(1)
$Tl_1\cdots O_2^{II}$	3.25(1)	$Tl_2\cdots O_3^{V}$	3.51(1)
$Tl_1\cdots O_1^{II}$	3.51(1)		
$Tl_1\cdots O_1^{I}$	2.81(1)		
$Tl_1\cdots O_4^{I}$	2.98(1)		
$O_1–C_4$	1.24(2)	$C_1–C_2$	1.41(2)
$O_2–C_4$	1.24(2)	$C_1–C_3$	1.37(3)
$O_3–C_5$	1.24(3)	$C_2–C_3'$	1.43(3)
$O_4–C_5$	1.27(3)		
$C_1–C_5$	1.52(3)		
$C_2–C_4$	1.49(3)		
Type^{a-d}	Angle (°)	Type^{a-d}	Angle (°)
$C_2C_1C_3$	122(2)	$C_1C_3C_2'$	122(2)
$C_2C_1C_5$	120(2)	$O_1C_4C_2$	125(2)
$C_3C_1C_5$	118(1)	$O_1C_4C_2$	116(2)
$C_1C_2C_4$	124(2)	$O_2C_4C_2$	118(2)
$C_1C_2C_3'$	117(2)	$O_3C_5O_4$	124(2)
$C_4C_2C_3'$	119(2)	$O_3C_5C_1$	119(2)
		$O_4C_5C_1$	117(2)

[a] The numbers in parentheses are e.s.d.s in the last significant digit. [b] Atoms are labeled in agreement with Figs. 1 and 2. [c] Atoms labeled with a prime (′) are related to nonprimed atoms by the symmetry operation $1-x$, $1-y$, $1-z$. [d] Atoms labeled with a superscripted Roman numeral are related to those without Roman numerals by the following symmetry operations: I, $1\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$; II, $1\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; III, $1+x$, y, z; IV, $\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; V, $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$.

between the thallium ions and the carboxylate oxygens [11]. Coordination numbers higher than eight have been reported for thallium(I) but are not common [12, 13].

Supplementary Material

Listings of the final atomic coordinates and other data relevant to the structure are available from the authors on request.

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