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MONOALKYLTHALLIUM(III) DERIVATIVES: PREPARATION AND X-RAY CRYSTAL STRUCTURE OF CYCLOPROPYLBIS(ISOBUTYRATO)THALLIUM(III)

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Summary

Cyclopropylbis(isobutyrato)thallium(III) has been synthesised and its crystal structure determined. The compound crystallises in the orthorhombic space group $Pna2_1$, with a 7.316, b 12.079, c 16.19 Å. Linear polymers are present in which thallium is seven-coordinate. Two types of carboxylate ligands are present; one weakly chelating and the other both chelating and bridging.

This structure allows clarification of infrared spectroscopic data, presented for mono- and diorganothallium(III) carboxylates, in the solid state and in solution.

Introduction

Synthetic procedures are now available for several types of monoorganothallium species, $RTlX_2$ (R = aryl [1]; vinyl [2]; norbornane derivatives [3]; and groups of the types $ClCH_2$ [4], $(CH_3)_3SiCH_2$ [5], $(pyH^+Cl^-)CH_2$ [6], $PhCH(OCH_3)CH_2$ [7]; X = anionic species). In contrast to this wide range of stable derivatives, monoalkylthallium(III) compounds appear to have been reported with only four types of alkyl group; R = CH_3 [8—16], C_2H_5 [8,9,12,13,16], n-C_3H_7 [12] and $(CH_3)_3CCH_2$ [17]. A variety of potentially bidentate [8,9], quadridentate [15] and quinquidentate [16] anionic ligands has been used to stabilise these monoalkyl compounds but the precursor compounds [8,14] (where X = carboxylate for R = CH_3, C_2H_5, n-C_3H_7) and $([CH_3)_2CCH_2]_2TlBr$ [17] are apparently less stable in solution and in the solid state. As part of an investigation of monoalkylthallium(III) compounds we have isolated the cyclopropyl derivative, $C_3H_5Tl[OCOCH(CH_3)_2]_2$ (I), which appears to be remarkably stable.

Little is known about the structures of monoorganothallium(III) compounds. The two available structure determinations are of complexes of CH_3Tl^{2+} with quadri- [15] and quinqui-dentate [16] ligands respectively. The structures involving these multidentate ligands give little indication of the preferred co-ordination around thallium in the precursor monoalkylthallium(III) carboxylates. Our previous attempts to isolate crystalline samples of (alkyl)-TlX_2 (X = $OCOCH_3$, $OCOCH(CH_3)_2$) failed due to crystal disintegration on removal of solvent during isolation of the products. The cyclopropyl derivative, I, proved exceptional in this respect, and an X-ray crystal structure determination was therefore undertaken.

Experimental

Preparation of dicyclopropylbromothallium(III). Cyclopropylmagnesium bromide [18] (0.13 mol) in THF (100 cm^3) was added slowly (45 min) with stirring to a cooled (—20° C) freshly prepared solution of thallium(III) bromide [2a] (0.06 mol) in THF (100 cm^3) under dry nitrogen. Stirring was continued for a further 20 min at —20° C and then, after being allowed to warm to room temperature, the mixture was hydrolysed with aqueous ammonium bromide solution (5%). The crude product was collected by filtration, washed with water and ether and dried over P_2O_5. Extraction of this material (14.5 g) with pyridine (500 cm^3) at 45° C and concentration to ca. 25 cm^3, followed by addition of petroleum ether, gave the product as a white solid. (Found: C, 20.2; H, 2.8. $C_6H_{10}TlBr$ calc.: C, 19.7; H, 2.7%.)

Preparation of dicyclopropylisobutyratothallium(III). Dicyclopropylbromothallium(III) (5.0 mmol) and isobutyratosilver(I) (4.6 mmol) were mixed in methanol solution. Silver bromide was removed by filtration, and evaporation of the solvent gave the product as a white solid (75%), which was used without further purification.

Preparation of cyclopropylbis(isobutyrato)thallium(III), I. A solution of dicyclopropylisobutyratothallium(III) (0.8 g; 0.002 mol) and bis(isobutyrato)-mercury(II) (0.8 g; 0.002 mol) in methanol (100 cm^3) was stirred for 4 h. The mixture was filtered and evaporation of the filtrate at 30° C under reduced pressure gave a white solid. The mercury salts were removed by washing with benzene (50 cm^3). Recrystallisation from methanol gave I (0.4 g; 44%) as colourless needles. (Found: C, 31.6; H, 4.6. $C_{11}H_{19}O_4Tl$ calc.: C, 31.5; H, 4.5%.)

Dimethylacetatothallium(III) and methylbis(acetato)thallium(III) were prepared as previously reported [8].

Physical measurements

Microanalyses were carried out by the Butterworth Microanalytical Service, London. IR spectra were recorded on a Pye Unicam SP2000 spectrophotometer as mulls in Nujol and HCB, and in chloroform solution.

Crystallography

Weissenberg photographs of I indicated orthorhombic symmetry. The systematically absent reflections were those required for either the space group

Pna2_1 or *Pnma*. The non-centrosymmetric space group, *Pna*2_1, was found to be the correct one.

Unit cell calibration was carried out for the sample by a least squares fit of the angular parameters for 25 reflections with 2θ ca 20° on a Philips PW1100 automatic four-circle diffractometer using graphite monochromatised Mo-K_α radiation (γ 0.7107 Å). A $\theta - 2$ scan mode was used for data collection and reflections with $3.0 \leqslant \theta \leqslant 26.0°$ were examined. Weak reflections which gave $I_t - 2(I_t)^{1/2} < I_b$ on the first scan were not further examined. (I_t is the intensity at the top of the reflection peak and I_b is the mean of two preliminary 5 s background measurements on either side of the peak.) Of the remaining reflections, those for which the total intensity recorded in the first scan of the peak (I_i) was <500 counts were scanned twice to increase their accuracy. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.70 + 0.05 \tan \theta)°$ was used, with a background measuring time proportional to I_b/I_i. Three standard reflections were measured every 6 h. These showed a decrease of ca. 21% during data collection and were used to scale the data to a common level. See Table 1 for pertinent crystal information and details of data collection.

Reflections in an octant (761) were measured after the preliminary test (see above). The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer [19]. The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error [20]. I and $\sigma(I)$ were corrected for Lorentz and polarisation factors and reflections for which $I \leqslant 3\sigma(I)$ were rejected. The transmission factors estimated for the crystal along the non-equivalent edge lengths were (0.336) and (0.065). No absorption corrections were applied. Equivalents were averaged to give 749 unique reflections of which 54 were considered to be unobserved. The structure was solved by the heavy atom method and refined by full matrix least-squares.

The Patterson function and an initial difference map were solved in the centrosymmetric space group *Pnma* and showed peaks corresponding to an isobutyrate ligand lying on a mirror plane and a second isobutyrate ligand oblique to the mirror plane, inconsistent with the space group symmetry elements. Subsequent difference maps with the non-centrosymmetric space group *Pna*2_1 revealed all the atom positions and the presence of disorder both in the methyl groups of the isobutyrate ligands and in one atom of the cyclopropane ring. See Fig. 1 for the atom labelling scheme. Two positions for C(2) [C(2a), C(2b)] and for C(7)

TABLE 1

SUMMARY OF CRYSTAL DATA AND INTENSITY COLLECTION FOR CYCLOPROPYLBIS(ISOBUTYRATO)THALLIUM(III)

Formula weight	419.4	Z	4
Space group	*Pna*2_1	$F(000)$	792
a (Å)	7.316	Crystal dimensions (mm)	0.1 × 0.1 × 0.25
b (Å)	12.079	μ (cm^{-1})	108.90
c (Å)	16.119	Final no. of variables	82
V ($Å^3$)	1424.43	Unique data used, $I > 3\sigma(I)$	695

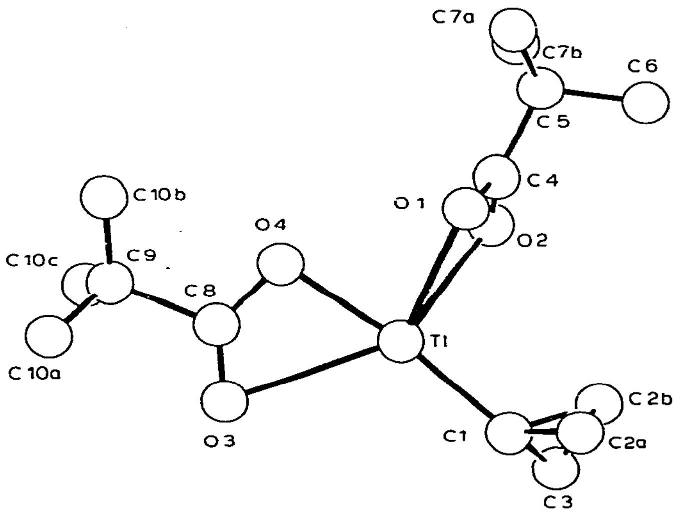


Fig. 1. The structure of I showing the disorder in atoms C(2), C(7), and C(10).

[C(7a), C(7b)] were found, together with a three-fold disorder for the atoms C(10) and C(11) [C(10a), C(10b), C(10c)]. It was necessary to constrain isotropic thermal parameters to be equal for the disordered sets of atoms. Based on these restrictions $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.045. However, the bond lengths obtained from this model were not chemically reasonable within the

TABLE 2

FINAL FRACTIONAL COORDINATES (Tl × 10^5; C, O × 10^4) AND ISOTROPIC THERMAL PARAMETERS (× 10^3) FOR I [a]

Atom	*x*	*y*	*z*	*U* (Å^2)	s.o.f. [b]
Tl	—1130	—6260	25000	[c]	1
O(1)	591(25)	674(11)	1061(40)	86(10)	1
O(2)	234(19)	740(9)	4004(37)	65(7)	1
O(3)	—1994(16)	—1549(14)	2333(68)	95(8)	1
O(4)	—1744(15)	—145(12)	2754(128)	89(5)	1
C(1)	1447(23)	—1275(22)	2707(102)	107(10)	1
C(3)	2411(28)	—822(20)	2269(75)	117(15)	1
C(4)	513(21)	1113(16)	2522(44)	74(6)	1
C(5)	763(23)	2047(17)	2230(92)	100(11)	1
C(6)	2023(26)	2123(26)	2301(137)	145(18)	1
C(8)	2308(28)	839(21)	2257(220)	93(14)	1
C(9)	—3670(27)	—660(19)	2412(53)	151(14)	1
C(2a)	2258(56)	—1128(45)	4056(86)	72(15)	1/2
C(2b)	2117(55)	—1525(38)	1226(102)	72(15)	1/2
C(7a)	270(59)	2499(65)	3885(105)	110(20)	1/2
C(7b)	341(60)	2459(67)	485(101)	110(20)	1/2
C(10a)	—4211(46)	—1290(23)	3431(56)	102(10)	2/3
C(10b)	3986(47)	—723(24)	548(42)	102(10)	2/3
C(10c)	3988(40)	129(22)	3097(63)	102(10)	2/3

[a] Values of e.s.d.'s in parentheses. [b] Site occupation factor. [c] Anisotropic thermal parameters (× 10^3) for Tl: U_{11}, 67(0); U_{22}, 84(0); U_{33}, 57(0); U_{12}, 0(0); U_{13}, 9(1); U_{23}, —1(5).

disordered parts of the molecule, with chemically equivalent bonds showing a long/short pattern with average values at the expected values.

The chemically equivalent distances in the disordered parts of the molecule were then constrained to be equal within an e.s.d. of 0.005 Å by the addition of extra observational equations to the least-square matrix [21]. The bond lengths were initially set at the average values obtained from the previous model and acceptable values were then obtained at completion of refinement. In the final cycle of refinement the mean and maximum shift/σ were (0.33) and (1.58) respectively. The final R was 0.045 and R_w = 0.050 where: $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; with $w = 0.8247(\sigma^2|F_o| + 2.045 \times 10^{-3}|F_o|^2)^{-1}$. Neutral atom scattering factors were used [22], and those for Tl were corrected for anomalous dispersion effects ($\Delta f'$, $\Delta f''$) [23]. Computation was carried out using the SHELX [21] system and ORTEP2 [24]. A list of the observed and calculated structure amplitudes for the data used in the refinements is available from the authors. The final atomic positional and thermal parameters are listed in Table 2.

Results and discussion

Cyclopropylbis(isobutyrato)thallium(III), I, was obtained as colourless crystals from dicyclopropylisobutyratothallium(III) by an exchange reaction with bis(isobutyrato)mercury(II) in a manner similar to that described for the preparation of other monoalkylthallium(III) carboxylates [8,12]. The crystals were suitable for X-ray crystal structure analysis and the results obtained represent the first available for a monoorganothallium(III) derivative with a simple anionic ligand. Structural details for only one other cyclopropyl—metal derivative, $Al_2(C_3H_5)_6$, appear to have been published [25].

A view of I illustrating the disorder observed and the atomic numbering scheme is shown in Fig. 1. The principal bond lengths and angles are listed in Table 3 and the co-ordination geometry around thallium is shown in Fig. 2. The $C_3H_5Tl(O_2C_4H_7)_2$ units exist in the crystal as infinite linear polymers in which one of the isobutyrate groups, while chelating the Tl atom, also forms oxygen bridges to the Tl atoms of adjacent units. A section of the polymer chain is shown in Fig. 3.

In the $C_3H_5Tl(O_2C_4H_7)_2$ unit (Fig. 1) the thallium atom is five co-ordinate. Polymerisation via the bridging oxygen atoms, however, increases the co-ordination to seven (Fig. 2). The co-ordination geometry of the Tl atom is irregular but may be derived from a pentagonal bipyramid by bending the equatorial atom O(3) towards the O(4) axial position. Seven co-ordinate thallium is unusual but has been found previously in dimethylxanthegenatothallium(III) [26], although bridging S—Tl distances of 3.19 to 3.35 Å were found compared to S—Tl distances of 2.96 Å within the planar TlS_2C unit. In the case of $[C_3H_5Tl(O_2C_4H_7)_2]_n$ the bridging O—Tl distances are not overly long (2.57 to 2.67 Å) compared to the chelating O—Tl distances of 2.50 Å within the same isobutyrate group. The Tl—Tl distance between adjacent monomer units is 4.187 Å.

The non-bridging isobutyrate ligand acts as a weak chelate to the thallium atom, showing considerable ester-type character with two very different O—Tl distances of 2.12 and 2.71 Å to oxygen atoms O(4) and O(3) respectively. The

TABLE 3

INTERATOMIC DISTANCES AND ANGLES FOR I [a]

Distances [b]

O(1)—C(4)	1.285(16)	C(1)—C(2a)	1.410(30) [c]	C(5)—C(7b)	1.527(30) [c]
O(2)—C(4)	1.285(16)	C(1)—C(2b)	1.410(30) [c]	C(8)—C(9)	1.675(45)
O(3)—C(8)	1.207(32)	C(4)—C(5)	1.550(35)	C(9)—C(10a)	1.419(28) [c]
O(4)—C(8)	1.359(61)	C(5)—C(6)	1.527(28)	C(9)—C(10b)	1.420(28) [c]
C(1)—C(3)	1.411(30) [c]	C(5)—C(7a)	1.533(27) [c]	C(9)—C(10c)	1.419(28) [c]

Angles [d]

C(1)—C(3)—C(2a)	60.0(3)	Tl—C(1)—C(2a)	125.0(49)
C(1)—C(3)—C(2b)	60.0(3)	Tl—C(1)—C(2b)	125.8(49)
C(1)—C(2a)—C(3)	60.0(3)	O(1)—Tl—O(2)	52.2(6)
C(1)—C(2b)—C(3)	60.0(4)	O(4)—Tl—O(3)	55.2(7)
C(3)—C(1)—C(2a)	60.0(3)	C(1)—Tl—O(1)	98.0(13)
C(3)—C(1)—C(2b)	60.0(3)	C(1)—Tl—O(4)	168.3(26)
C(4)—C(5)—C(6)	105.5(27)	C(1)—Tl—O(3)	117.9(10)
C(4)—C(5)—C(7a)	106.1(56)	C(1)—Tl—O(2)	104.4(13)
C(4)—C(5)—C(7b)	118.2(55)	O(1)—Tl—O(3)	136.5(11)
C(8)—C(9)—C(10a)	111.4(43)	O(2)—Tl—O(4)	78.2(13)
C(8)—C(9)—C(10b)	100.7(63)	O(1)—Tl—O(4)	92.6(13)
C(8)—C(9)—C(10c)	116.4(36)	O(2)—Tl—O(3)	130.0(9)
C(10a)—C(9)—C(10b)	109.2(13) [e]	O(1^{ii})—Tl—O(1)	120.6(6)
C(10a)—C(9)—C(10c)	109.3(13) [e]	O(1^{ii})—Tl—O(2)	68.4
C(10b)—C(9)—C(10c)	109.3(13) [e]	O(1^{ii})—Tl—O(3)	81.2(11)
O(1)—C(4)—O(2)	117.6(22)	O(1^{ii})—Tl—O(4)	74.0(13)
O(1)—C(4)—C(5)	114.0(32)	O(1^{ii})—Tl—C(1)	96.1(13)
O(2)—C(4)—C(5)	128.5(33)	O(1^{ii})—Tl—O(2^{i})	163.3(6)
O(3)—C(8)—O(4)	127.7(56)	O(2^{i})—Tl—O(1)	70.1(6)
O(3)—C(8)—C(9)	117.9(31)	O(2^{i})—Tl—O(2)	120.7(6)
O(4)—C(8)—C(9)	109.4(41)	O(2^{i})—Tl—O(3)	82.5(9)
C(6)—C(5)—C(7a)	108.8(11) [e]	O(2^{i})—Tl—O(4)	93.5(13)
C(6)—C(5)—C(7b)	109.0(12) [e]	O(2^{i})—Tl—C(1)	94.9(13)
Tl—C(1)—C(3)	117.0(29)		

[a] The supercripts i and ii refer to the symmetry transformations $-x$, $-y$, $-1/2+z$ and $-x$, $-y$, $1/2+z$ respectively (see Fig. 3). [b] In Å; e.s.d.'s in parentheses. [c] Constrained bond lengths. [d] In degrees; e.s.d's in parentheses. [e] Constrained angles.

shorter of these two bonds makes an angle of 168° with the Tl—C bond to the cyclopropyl ring and strikingly demonstrates that the dominant characteristic of dialkylthallium(III) chemistry whereby thallium tends to form a near-linear arrangement with two strongly bonded groups [1a, 26—28] persists into monoalkylthallium(III) systems. Indeed, the polymeric pattern of I is very similar to that found for dimethylacetatothallium(III), $(CH_3)_2TlO_2CCH_3$ [28], and the structural arrangement of I can be considered to be derived from the latter by replacing one of the alkyl groups with the non-bridging isobutyrate group. The C—Tl—C angle in $(CH_3)_3TlO_2CCH_3$ is 172(2)° [28] (cf. C(1)—Tl—O(4) in I 168(3)°). The least squares plane through O(1), O(2), C(4), C(5), Tl of the bridging ligand and that through O(3), O(4), C(8), C(9), Tl of the non-bridging ligand intersect at an angle of 78° (see Table 4). This is close to the angle (86°) made between the Tl—CH_3 bond and the TlC_2O_2 plane of the chelating and bridging acetate ligand in dimethylacetatothallium(III).

The Tl—C bond length of 2.160 Å is similar to that found in the two other reported structures of monoalkylthallium(III) compounds (Tl—C = 2.147 Å in

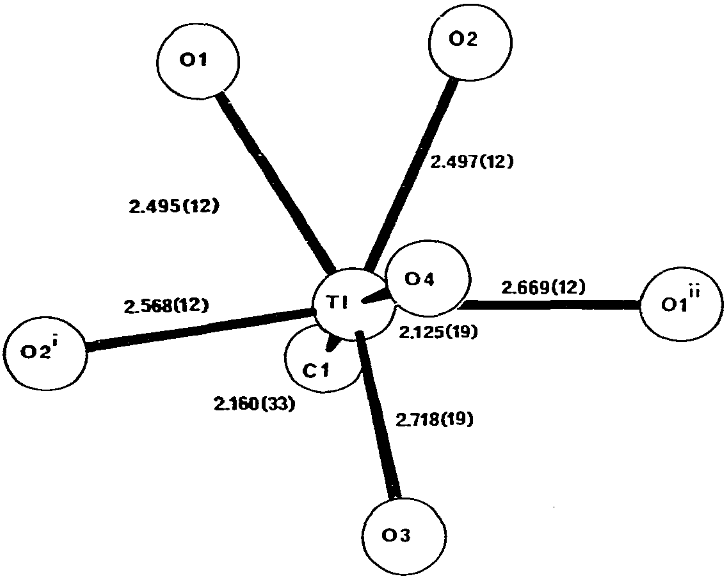


Fig. 2. Coordination geometry around Tl in I showing bond lengths (Å) with e.s.d.s. in parentheses. (See footnote to Table 3 for definitions of superscripts i and ii.)

methyl-5,10,15,20-tetraphenylporphinatothallium(III) [15]; Tl—C = 2.073 Å in a methylthallium(III) complex of 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine [16]). The Tl—C distance in I also in the range (2.01—2.20 Å) found

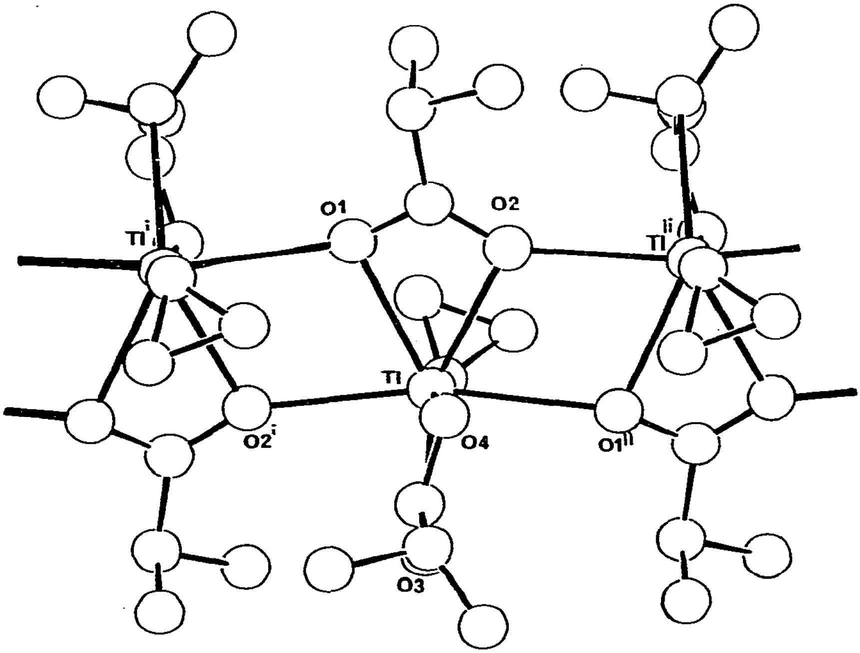


Fig. 3. A section of the polymer chain in I. For clarity, only one position for each disordered atom is shown. (See footnote to Table 3 for definitions of superscripts i and ii.)

TABLE 4

LEAST SQUARES PLANES DEFINED BY $lx + my + nz = p$

Plane	Atoms defining plane	l	m	n	p
1	O(1), O(2), C(4), C(5), Tl	—0.954	0.227	—0.196	—0.522
2	O(3), O(4), C(8), C(9), Tl	0.020	0.127	—0.992	—1.983

Deviations from planes (Å)

1 O(2),—0.064; O(2), —0.051; C(4), 0.023; C(5), 0.073; Tl, 0.065

2 O(3), —0.076, O(4), —0.088; C(8), 0.117; C(9), 0.007; Tl, 0.038

Angle between planes 78.3°

for Tl—C bonds in neutral dialkylthallium(III) species [26—28].

The short C—C distances found in the cyclopropyl group (1.41 Å) are a result of the crystallographic treatment of the disorder and are not comparable to the values found in other monosubstituted cyclopropyl derivatives.

Infrared spectra

The role of the carboxylate anions (bridging and/or chelating) in organothallium(III) carboxylates has previously been suggested from assignments of their IR spectra [8,11,29—31]. Consideration of the structure of I, together with that of $(CH_3)_2TlO_2C_2H_3$ [28] allows clarification of these interpretations.

The IR spectra in the region 1350—1650 cm^{-1} for I and other alkylthallium(III) carboxylates are compared in Tables 5 and 6, and the bands are assigned as $\nu(CO_2)$ asymmetric or symmetric stretching frequencies. The spectra indicate that the monoalkylthallium(III) compounds have similar structures in the solid state. Likewise, the solid state structures of $(CH_3)_2TlO_2C_2H_3$ and $(C_3H_5)_2TlO_2C_4H_7$ appear to be similar. The crystal structure of $(CH_3)_2TlO_2C_2H_3$ shows only one type of acetate group [28], and this is both chelating and bridg-

TABLE 5

IR ABSORPTION BANDS IN THE REGION 1350—1650 cm^{-1} OF ALKYLTHALLIUM(III) CARBOXYLATES IN THE SOLID STATE [a, b]

$C_3H_5TlX_2$ (I)	$(C_3H_5)_2TlX$	CH_3TlX_2 [c]	CH_3TlY_2 [d]	$(CH_3)_2TlY$ [e]	Assignment [f]
1615s		1610s	1610s		$\nu(CO_2)$*asym.*
1512vs	1528s	1510s	1539s	1540vs(br)	
1505vs(sh)	1518s(sh)				
1480w					
1471w	1468w	1468m			$\nu(CO_2)$*sym.*
1428s	1411s	1425s		1428vs(br)	
			1420—1380s(br)		
1390m		1390s			
1377w		1372m			
1360w	1360m	1359m			

[a] X = $O_2C_4H_7$; Y = $O_2C_2H_3$. In cm^{-1}. vs very strong, s strong, m medium, w weak, sh shoulder, br broad. [b] Spectra obtained using Nujol or hexachlorobutadiene mulls. [c] Data from ref. 8. [d] Band positions in agreement with those in ref. 11. [e] Band positions in good agreement with those in refs. 11, 29 and 30. [f] Assignments by analogy with, or as given in refs. 8, 11, 29—31.

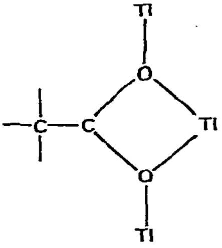
TABLE 6

IR ABSORPTION BANDS IN THE REGION 1350—1650 cm^{-1} OF ALKYLTHALLIUM(III) CARBOXYLATES IN SOLUTION [a, b]

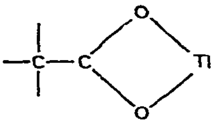
$C_3H_5TlX_2$ (I)	$(C_3H_5)_2TlX$	CH_3TlX_2 [c]	CH_3TlY_2	$(CH_3)_2TlY$	Assignment [d]
1590s(br,sh)		1577(br)	1590s(sh)		$\nu(CO)_2asym.$
1540s(br)	1545s(br)	1525s	1560s(br)	1570s	
1473m	1480w	1469s			
1408m	1420m	1405s	1415s(br)	1428s(br)	$\nu(CO_2)sym.$
1395(sh)		1400(sh)	1387(sh)		
1375m	1375w	1370m			
1365m		1360m			

[a] See footnote a, Table 5. [b] Spectra obtained in $CHCl_3$ solution, 1% w/w. [c] Data from ref. 8. [d] Assignment by analogy with, or as given in, ref. 8.

ing (A). A simultaneously chelating and bridging carboxylate anion is also



(A)



(B)

found in the structure of I. This indicates that for all the alkylthallium(III) carboxylates in Table 5, strong bands in the regions 1505—1540 and 1411—1428 cm^{-1} can be assigned as $\nu(CO_2)asym.$ and $\nu(CO_2)sym.$ respectively in chelating and bridging anions of type A. The additional strong bands in the regions 1610—1615 and 1380—1390 cm^{-1} for the monoalkylthallium(III) carboxylates are consequently assigned as $\nu(CO_2)asym.$ and $\nu(CO_2)sym.$ respectively in chelating carboxylates (B) as found in the structure of I. The higher energies of the $\nu(CO_2)asym.$ bands of structural type B are consistent with the lack of bridging function and, as indicated by the structure of I, with the significantly ester-type character of this group.

On dissolution in chloroform $\nu(CO_2)asym.$ for ligands of type A increases by 15—35 cm^{-1}, consistent with partial disruption of bridging Tl—O bonds as solvent molecules break up the polymer chains. This interpretation is also consistent with the state of aggregation (ca. 2) of $CH_3Tl(OC_4H_7)_2$ in $CHCl_3$ solution [8]. The values of $\nu(CO_2)asym.$ for ligands of type B decrease by 20—33 cm^{-1} for chloroform solutions, and this may be due to ester-like arrangement in B being altered to for a more symmetrically coordinated carboxylate anion.

The IR spectra of other organothallium(III) carboxylates have been reported ($C_2H_5TlX_2$, $(C_2H_5)_2TlX$ [8], $C_6H_5TlX_2$ [31], $C_6H_5TlY_2$ [11,31], $(C_6F_5)_2TlY$ [29]; $X = O_2C_4H_7$; $Y = O_2C_2H_3$) and the similarity of their spectra (in the region 1350—1650 cm^{-1}) to those in Table 5 suggests that they contain carboxylate anions of type A and, for the mono-organothallium(III) species, also type B.

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