Structures of Complexes of Thallium(I) and Functionalized Benzoate Ligands with Pronounced Stereoactivity of the Lone Pair of Electrons and Metal−Phenyl π-Bonding

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Keywords: Thallium(I) / Stereoactive inert pair / Thallophilic interaction / Coordination polymer / Metal−phenyl π-bonding

Four complexes between thallium(I) and functionalized benzoate ligands, namely salicylate, *p*-aminosalicylate, 3,4-dimethoxybenzoate and 3,5-dimethoxybenzoate have been prepared and their structures determined by X-ray diffraction. They are all based on dimeric, centrosymmetric $Tl_2(RCOO)_2$ units with μ_2-bridging carboxylic groups resulting in Tl···Tl separations of 4.2–4.4 Å. These dimeric units are further linked to form infinite coordination polymers. In *catena*-[bis(μ_3-salicylato)dithallium(I)] (**1**) and *catena*-[bis(μ_3-4-aminosalicylato)dithallium(I)] (**2**) are adjacent units are held together by secondary Tl–O(hydroxy) interactions resulting in a crystal organization which can be described as stair-like, infinite one-dimensional polymers. In *catena*-[μ_4-(3,4-dimethoxybenzoato)thallium(I)] (**3**) bridges each carboxylic group four thallium(I) cations resulting in infinite two-dimensional, puckered sheets. Finally, in *catena*-[μ_3-(3,5-dimethoxybenzoato)thallium(I)] (**4**) each carboxylic unit acts as a μ_3-bridging ligand to give nearly planar, infinite double-stranded arrays of Tl^+ cations. Another characteristic structural motif is the tendency of the thallium ion to only use less than one hemisphere to coordinate ligands. This "half-nakedness" is due to the stereochemically active inert pair ($6s^2$), which thus plays a prominent role in controlling the structures of these compounds. The Tl^+ cations are in approximate pyramidal geometries, with four or five oxygen donor atoms in the basal plane and the stereoactive lone pair occupying the apex position of the pyramid. There are, on the naked side of the metal ions, relatively large spaces in nonpolar environments provided by neighboring phenyl groups. The distances between the planes of the phenyl rings and the Tl^+ cation are in the range 3.3–3.5 Å, indicating that Tl^+–phenyl η^6-interactions are important in the crystal organization.

Introduction

The Tl^+ ion is nonspherical, with its inert pair ($6s^2$) partially hybridized leading to the formation of a local dipole that may strongly affect cation···ligand interactions. This "inert-pair effect" has, in a general way, been explained by Pitzer[1] and by Pykko and Desclaux[2] as a relativistic effect causing the outer s electrons to be more strongly attracted to the nucleus than normally expected. In p-block cations with an ns^2 np^0 electronic configuration, lone pairs of electrons may thus play a prominent role in controlling the structures and chemical behavior. In inorganic salts, the lone pair is manifested by a distortion of regular coordination geometries by a substantial elongation of certain bonds, as exemplified in, for example, TlF,[3] $Tl[CuAsO_4]$, $Tl[CuPO_4]$[4] or $TlZn(PO_3)_3$.[5] In several organometallic compounds, the stereoactive lone pair is manifested by a "half-naked" cation, with ligands only coordinating one hemisphere, as observed in the crystal structures of complexes between Tl^+ and tris(pyrazolyl)borate, where the lone pair occupies the fourth position of a tetrahedron bis(pyrazolyl)phosphinate,[6] with an obvious gap in the coordination sphere due to the lone pair, and also in [HB(3-*p*-tolylpyrazolyl)$_3$Tl].[7] In (malonohydroxamato)Tl, a square-pyramidal geometry of Tl^+ is observed, with the lone pair oriented in the axial direction.[8] In addition, in several organometallic thallium compounds the stereoactivity of the inert pair is apparent.[9]

There is a paucity of data on complexes between thallium(I) and arylcarboxylate ligands in the literature, the only known example being *catena*-[bis(μ_3-2-hydroxybenzoato)dithallium(I)].[10] In this paper we wish to present the crystal structures of four complexes between thallium(I) and functionalized benzoate ligands, namely salicylate (**1**), 4-aminosalicylate (**2**), 3,4-dimethoxybenzoate (**3**) and 3,5-dimethoxybenzoate (**4**) (Scheme 1). These ligands present a limited range of steric and electronic properties and are therefore useful for establishing basic patterns in thallium(I)−benzoate interactions. In following papers, we wish to extent these investigations to systems where steric requirements of the ligands impose restrictions on the thallium coordination geometries and also attempt the use of

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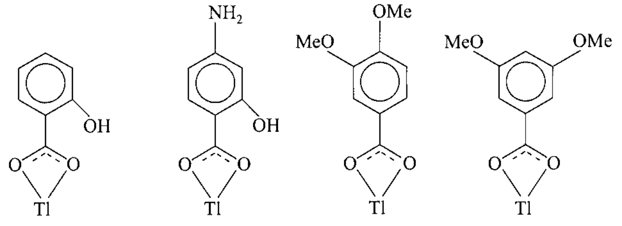

1 2 3 4

Scheme 1. Monomeric units of compound **1**−**4**

the inert lone pair as a Lewis base for the construction of extended solids.

Results and Discussion

catena-[Bis(μ_3-salicylato)dithallium(I)] (1) − Crystal Structure

The crystal structure is based on dimeric units as depicted in Figure 1. The carboxylate groups act as μ_2-bridging ligands. One oxygen atom is bound to two thallium ions and the other to one thallium ion. The doubly coordinated O1 bridges thallium ions unsymmetrically with Tl−O distances of 2.601(11) and 2.751(11) Å and a Tl−O−Tl angle of 103.8(4)°. The O1^{i}−Tl1−O1 and O1−Tl1−O2 angles equal 76.2(4) and 48.4(3)°, respectively. The singly coordinated O2 has a Tl−O distance of 2.778(11) Å. This geometry results in a Tl···Tl separation of 4.213(1) Å. Each Tl^+ ion is coordinated on one side to three oxygen atoms of two carboxylic groups and, at a longer distance, to one O3 atom of adjacent units. The other side is, however, completely "naked" due to the inert pair ($6s^2$) in an sp-hybridized orbital producing an electronic bulge on this side. Each Tl^+ cation is therefore in a distorted square-pyramidal geometry, with the four oxygen atoms in the basal plane and the stereoactive lone pair occupying the apex position of the pyramid (Figure 2). The Tl^+ ion is situated 1.64 Å from the least-squares plane defined by the oxygen atoms. There is, on the "naked" side of the metal ion, a relatively large space in a hydrophobic environment provided by two neighboring phenyl groups. The distance between the planes of the phenyl rings and the Tl^+ cation is 3.29 Å. This value is similar to that of 3.27 Å in $[Tl(PhNNNPh)]_2$ and 3.33 Å in $[Tl(TolNNNNNTol)]_2$[11] or to that in a complex between Tl^+ and Lasalocid A, an ionophore containing a salicylic group, where a distance of 3.22 Å is observed.[12] These values fall essentially within the range of van der Waals distances [the sum of the ionic radius of Tl^+ (1.47 Å)[13] and the van der Waals radius of the aromatic ring (1.77 Å)[14]], which is 3.24 Å, thus indicating Tl^+−phenyl η^6-interactions. The aromatic ring is nearly perpendicular (87.1°) to the vector joining the Tl^+ cation and the centroid of the phenyl group.

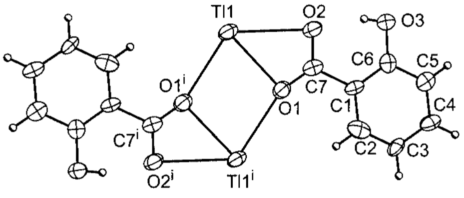

Figure 1. Molecular structure and atom numbering scheme for bis(salicylato)dithallium(I) (**1**); the displacement ellipsoids are drawn at the 50% probability level for non-H atoms; symmetry code: i: $-x$, $2 - y$, $2 - z$

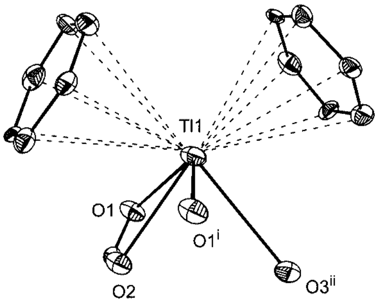

Figure 2. The coordination of the Tl^+ ion in **1** showing the stereoactivity of the lone pair; the geometry of the Tl^+ cation can be described as a distorted square-based pyramid, with the stereoactive lone pair occupying the apex position in a hydrophobic environment; the centroids of the phenyl rings are situated 3.29 Å from the Tl^+ cation; the displacement ellipsoids are drawn at the 50% probability level; bond lengths [Å]: Tl1−O1 2.601, Tl1−O2 2.778, Tl1−O1^{i} 2.751, Tl1−O3^{ii} 2.798; symmetry codes i: $-x$, $2 - y$, $2 - z$; ii: $x - 1$, y, z

The $Tl_2(COO)_2$ unit is virtually planar with a mean deviation from the least-squares plane of 0.0128 Å. The phenyl rings form an angle of 11.1° with this plane, resulting in an average deviation from the plane defined by all atoms of the $Tl_2(C_7H_5O_3)_2$ molecule of 0.125 Å. The $Tl_2(COO)_2$ units are stacked into piles along the *c* axis. The units are tilted 47.9° versus the *c* axis giving a parallel displacement of 5.77 Å with a perpendicular distance of 3.23 Å between successive units. The displacement of successive planes makes aromatic π-interactions unfeasible in the crystal organization. Adjacent units are held together by secondary Tl−O3 interactions [d(Tl−O3) = 2.978(11) Å], resulting in stair-like, infinite one-dimensional polymers as schematically depicted in Figure 3. The packing in the unit cell is shown in Figure 4.

catena-[Bis(μ_3-*ortho*-aminosalicylato)dithallium(I)] (2) − Crystal Structure

The molecular structure of bis(2-aminosalicylato)dithallium(I) (**2**) is shown in Figure 5. In this case the carboxylate groups act also as μ_2-bridging ligands with one oxygen atom unsymmetrically bridging two thallium ions [d(Tl−O) = 2.614(12) and 2.713(11) Å] and the other one to one thallium ion [d(Tl−O) = 2.879(12) Å] which results in a Tl−Tl separation of 4.253(1) Å. The Tl^+ ion is in a distorted square-pyramidal geometry, with the four oxygen atoms in the basal plane and the stereoactive lone pair oc-

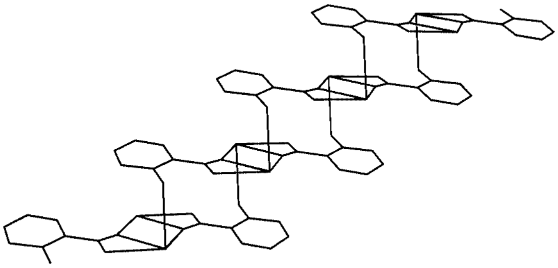

Figure 3. Schematic drawing of the crystal organization of **1**; each $Tl_2(C_6H_5OHCOO)_2$ unit is linked to adjacent units via two secondary Tl−O(hydroxy) interactions [*d*(Tl−O) = 2.97(1) Å]; successive units are parallel displaced by 5.77 Å producing a stair-like, infinite one-dimensional polymer

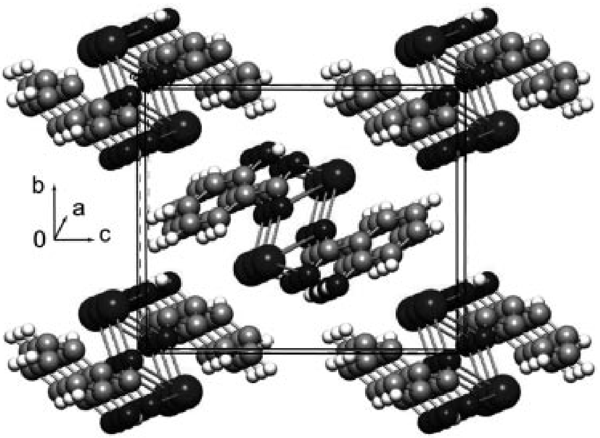

Figure 4. The unit cell content of **1** viewed along the crystallographic *a* axis

cupying the apex position of the pyramid, in a hydrophobic environment provided by two neighboring phenyl groups. The distance between the planes of the phenyl rings and the Tl^+ cation are 3.31 and 3.68 Å with angles of 87.2 and 62.7° between the aromatic plane and the vector joining the Tl^+ cation and the centroid of the phenyl group. In addition to the strong intramolecular hydrogen bond between O3 and O2 [*d*(O···O) = 2.53(2) Å] are also weak hydrogen bonds formed between the amino protons and O2 atoms of adjacent units [*d*(N···O) = 3.02(2) and 3.15(2) Å].

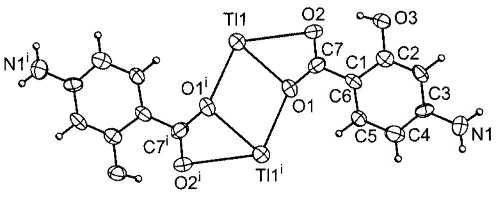

Figure 5. Molecular structure and atom numbering scheme for bis(2-aminosalicylate)dithallium(I) (**2**); the displacement ellipsoids are drawn at the 50% probability level for non-H atoms; symmetry code: i: −*x*, 2 − *y*, 2 − *z*

The crystal organization shows large similarities with that of compound **1**. The $Tl_2(COO)_2$ unit is slightly twisted with a mean deviation from the least-square plane of 0. 123 Å. The phenyl rings form an angle of 16.0° with this plane, resulting in an average deviation from the plane defined by all atoms of the $Tl_2(C_7H_5O_3)_2$ moiety of 0.217 Å. The $Tl_2(COO)_2$ units are stacked into piles along the *c* axis. The units are tilted 45.1° versus the *c* axis giving a parallel displacement of 6.00 Å. Adjacent units are held together by secondary Tl−O3 interactions [*d*(Tl−O3) = 2.923(11) Å]. The overall crystal organization can be described as stair-like, infinite one-dimensional polymers as depicted in Figure 3. The crystal structures of compounds **1** and **2** show certain similarities with that of a previous determination of *catena*-[bis(μ$_3$-2-hydroxybenzoato)dithallium(I)].[11] The dimeric unit in this compound shows a Tl−Tl separation of 4.129 Å and successive units are linked via Tl−O(hydroxy) interactions [*d*(Tl−O) = 2.727 Å] to give infinite polymers similar to those in Figure 3.

catena-[(3,4-Dimethoxybenzoato)thallium(I)] (3) − Crystal Structure

The crystal structure is based on dimeric $Tl_2(C_7H_6NO_3)_2$ units as shown in Figure 6. Each dimeric unit is extensively cross-linked to adjacent units to form an infinite two-dimensional network as schematically shown in Figure 7. One

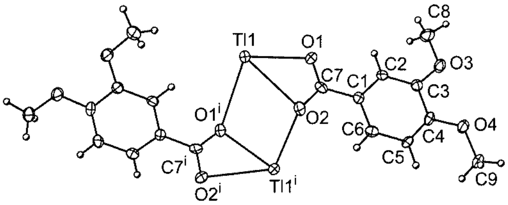

Figure 6. Molecular structure and atom numbering scheme for *catena*-[(3,4-dimethoxybenzoato)dithallium(I)] (**3**); the displacement ellipsoids are drawn at the 50% probability level for non-H atoms; symmetry code: i: −*x*, −0.5 + *y*, 0.5 − *x*

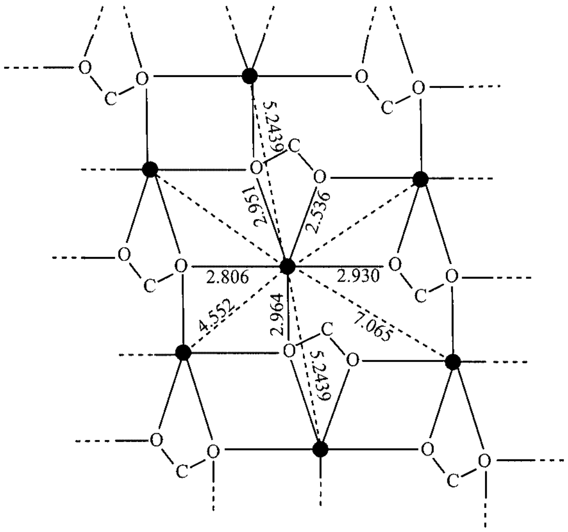

Figure 7. Schematic drawing of the crystal organization of **3**, which consists of infinite two-dimensional, puckered sheets of Tl^+ cations, linked by μ$_4$-bridging carboxylate groups

oxygen atom the carboxylate group is bound to three thallium ions and the other one to two thallium ions, with each carboxylate group acting as a μ$_4$-bridging ligand. The doubly coordinated oxygen atom O1 bridges two thallium ions unsymmetrically with Tl−O distances of 2.536(6) and 2.930(6) Å, while the triply coordinated O2 has a Tl−O distances of 2.806(7), 2.951(6) and 2.964(7) Å. As a result of this geometry each Tl$^+$ cation is surrounded by three other cations at comparatively short distances, two at 4.4111(8) Å and one at 4.552(1), and three cations at significantly longer distances, two at 5.244(1) and one at 7.065(1) Å. Each Tl$^+$ ion is coordinated on one side to five oxygen atoms of four carboxylic groups. In this case the other side is also completely naked due to the stereoactive lone pair. The geometry of the Tl$^+$ cation may be described as a distorted pyramid, with the five oxygen atoms in the basal plane and the stereoactive lone pair occupying the apex position of the pyramid, with the Tl$^+$ ion being situated 1.16 Å from the least-squares plane defined by the oxygen atoms. The phenyl rings form an angle of 46.0° with the Tl_2O_2 plane, resulting in an average deviation from the plane defined by all atoms of the $Tl_2(C_9H_9O_4)_2$ moiety of 0.692 Å. The crystal organization is shown in Figure 8. The infinite layers of Tl$^+$ cations extend perpendicular to the *a* axis, alternating with hydrophobic areas. The relatively large empty spaces, in hydrophobic environments, around one side of the Tl$^+$ cations are clearly seen.

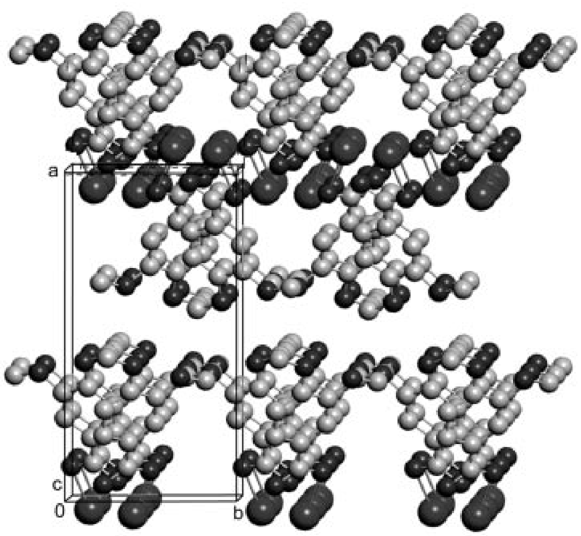

Figure 8. View parallel to the *c* axis of the packing of **3** in the unit cell; hydrogen atoms are omitted for clarity

catena-[(3,5-Dimethoxybenzoato)thallium(I)] (4) − Crystal Structure

The crystal structure is based on dimeric $Tl_2(C_9H_9O_4)_2$ units as shown in Figure 9. The Tl_2O_4 moiety is virtually planar, with a mean atomic displacement from the least-squares plane of 0.019 Å. This plane forms an angle of 7.5° with the aromatic planes which results in an average deviation from planarity for the entire $Tl_2(C_9H_9O_4)_2$ unit of 0.075 Å. The two Tl$^+$ ions are unsymmetrically bridged by the carboxylic oxygen atoms O1 and O1^i with Tl−O distances of 2.530(5) and 2.710(5) Å, respectively, and a Tl−O−Tl angle of 105.3(2) Å. The O2−Tl1 distance is 2.785(4) Å. This geometry results in a Tl−Tl separation of 4.1669(8) Å. Each Tl$^+$ ion is coordinated on one side to four oxygen atoms of three carboxylate groups. In this case the other side is also completely "naked" due to the inert pair (6s^2). The Tl$^+$ cation is therefore in a distorted square-pyramidal geometry, with the four oxygen atoms in the basal plane and the stereoactive lone pair occupying the apex position of the pyramid.

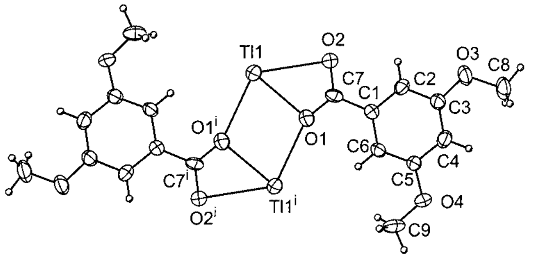

Figure 9. Molecular structure and atom numbering scheme for *catena*-[(3,5-dimethoxybenzoato)dithallium(I)] (**4**); the displacement ellipsoids are drawn at the 50% probability level for non-H atoms; symmetry code: i: $-x$, $1 - y$, $-x$

The dimeric $Tl_2(C_9H_9O_4)_2$ units are further linked to infinite one-dimensional chains as depicted in Figure 10. Each carboxylic unit acts as a μ$_3$-bridging ligand since the O2 oxygen atom links an adjacent unit with an O2−Tl1 distance of 2.720(6) Å. The result is a double-stranded, infinite linear one-dimensional polymeric array of Tl$^+$ cations with an average deviation from the plane defined by all Tl$^+$ cations within the chain of 0.014 Å. The chain forms an angle of 34.4° with the plane of the $Tl_2(C_9H_9O_4)_2$ unit. The closest separations between the Tl$^+$ cations within the chain are 4.1669(8) (within the basic unit), 4.2637(7) and 6.3813(9) Å (Figure 11). The chains run parallel to the *b* axis and the distance between adjacent chains is 5.55 Å. This arrangement results in the lamellar structure shown in Figure 12.

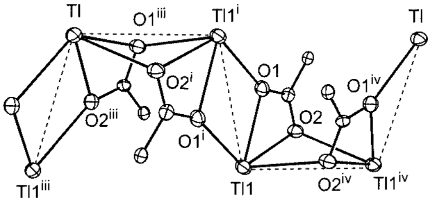

Figure 10. Part of one $[Tl_2(RCOO)_2]_n$ chain of **4** showing the μ$_3$-bridging mode of the carboxylate groups; phenyl groups are omitted for clarity; selected bond lengths [Å]: Tl1−O1 2.530(5), Tl1−O2 2.785(4), Tl−O1^i 2.710(5), Tl1−O2^{iv} 2.720(6); symmetry codes i: $-x$, $1 - y$, $-z$; ii: $-x$, $2 - y$, $-z$; iii: $-x$, y, $-z - 0.5$; iv: $-x$, y, $-z + 0.5$

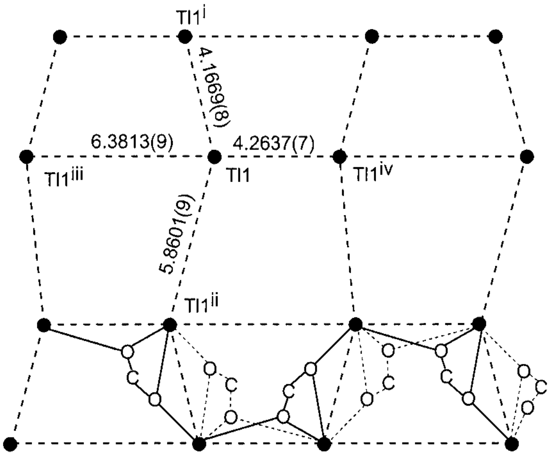

Figure 11. Schematic drawing of the crystal organization of **4** which consists of nearly planar, infinite arrays of Tl^+ cations linked by μ_3-bridging benzoate ligands; symmetry codes as in Figure 10

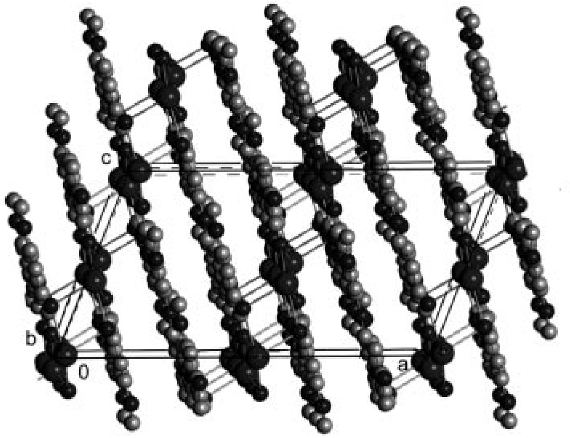

Figure 12. View of the extended lattice along the *c* axis of **4**; hydrogen atoms are omitted for clarity

Conclusions

The four complexes structurally determined in the present study, as well as (*o*-hydroxybenzoato)thallium(I) previously determined, are all based on centrosymmetric dimeric $Tl_2(RCOO)_2$ units. Geometrical parameters of this structural motif are summarized in Table 1. The carboxylate groups act as μ_2-bridging ligands within the unit. One oxygen atom is bound to two thallium ions and the other one to one thallium ion. The doubly coordinated oxygen atom bridges the thallium ions unsymmetrically with average Tl−O distances of 2.59(6) and 2.77(9) Å for the five thallium(I) benzoate compound so far structurally characterized. The singly coordinated oxygen atom has an average Tl−O distance of 2.79(6) Å. This geometry results in a Tl−Tl separation of 4.24(11) Å.

Another characteristic structural motif is the tendency of the thallium ion to only use less than one hemisphere to coordinate ligands. This "half-nakedness" is due to the stereochemically active inert pair ($6s^2$) in an sp-hybridized orbital producing an electronic bulge on one side. This lone pair of electrons thus plays a prominent role in controlling the structures of these compounds. The Tl^+ cations are therefore in pyramidal geometries, with four or five oxygen donor atoms in the basal plane and the stereoactive lone pair occupying the apex position of the pyramid. There are, on the "naked" side of the metal ions, relatively large spaces in a nonpolar environment provided by neighboring phenyl groups, with the nearest carbon atoms situated 3.2−3.4 Å from the Tl^+ ion. The aromatic rings are nearly perpendicular to the vector joining the Tl^+ cation and the centroid of the phenyl group, suggesting that Tl^+−phenyl η^6-interactions are of a certain importance for the crystal organization. Several other examples of structures with Tl^I−arene interactions have been presented, with comparable distances, as discussed by Janiak in his comprehensive review

Table 1. Geometry of the centrosymmetric $Tl_2(RCOO)_2$ moiety of five thallium(I)benzoate compounds

Compound:[a]		1	2	3	4	Ref.[11]	Average
Ligand:		Salicylate	4-Amino-salicylate	3,4-Dimethoxy-benzoate[b]	3,5-Dimethoxy-benzoate	3-Hydroxy-benzoate	
Tl1−O1	(Å)	2.601(11)	2.614(12)	2.536(6)	2.530(5)	2.663	2.59(6)
Tl1−O2	(Å)	2.778(11)	2.879(12)	2.806(7)	2.785(4)	2.775	2.79(6)
Tl1−O1^i	(Å)	2.751(11)	2.713(12)	2.930(6)	2.710(5)	2.727	2.86(9)
Tl···Tl	(Å)	4.213(1)	4.253(1)	4.4111(8)	4.1669(8)	4.129	4.23(11)
O1−Tl1−O2	(°)	48.4(3)	48.3(3)	47.2(1)	49.1(1)	48.4	48.3(7)
O1−Tl1−O1^i	(°)	76.2(4)	74.1(4)	68.0(1)	74.1(1)	79.2	74(4)
Tl1−O1−Tl1^i	(°)	103.8(4)	105.9(4)	100.0(2)	101.5(2)	100.8	102(2)
Tl1−Ph[c]	(Å)	3.276	3.312	3.417	3.474	3.265	−
Tl1−Ph[d]	(°)	87.1	87.2	84.0	79.2	89.3	−
Planarity[e]	(Å)	0.109	0.207	0.476	0.087	0.132	−
Twist[f]	(°)	11.0	16.0	45.4	9.5	12.8	−
Packing efficiency[g]	(%)	81.9	78.4	77.3	79.8	−	−

[a] Atomic numbering scheme as in Figures 1, 5 or 9. [b] Symmetry imposes a different numbering scheme as shown in Figure 6. [c] Distance between Tl1 and the centroid of the aromatic ring. [d] Angle between the plane of the aromatic ring and the vector joining Tl1 and the centroid of the aromatic ring. [e] Average atomic deviation from the least-squares plane defined by all atoms in the $Tl_2(C_6H_6COO)_2$ moiety. [f] Angle between the plane defined by the Tl1, Tl1^i, O1 and O2^i atoms and the plane defined by the benzoate ligands. [g] The fraction of the total cell volume occupied by atoms as determined by the Platon software.[19]

of thallium(I) chemistry.[15] The Tl−Tl distances observed in the present study, both within and between dimers, suggest a possible Tl···Tl metallophilic interaction, similar to the well-established aurophilic attraction.[16] Recent ab initio calculations on thallocene dimers suggests energy minima with Tl···Tl distances slightly under 4 Å and interaction strengths of the order of 10 kJ/mol.[17] This attractive interaction is due to dispersion mechanisms and can only be reproduced by ab initio calculations including explicit electron-electron correlation.

Despite the structural similarities, a large variation in crystal organization is observed. In *catena*-[bis(μ$_3$-salicylato)thallium(I)] (**1**), *catena*-[bis(μ$_3$-4-aminosalicylato)thallium(I)] (**2**) and *catena*-[bis(μ$_3$-2-hydroxybenzoato)thallium(I)][10] are adjacent units are held together by secondary Tl−O(hydroxy) interactions, with an average Tl−O distance of 2.96(3) Å, resulting in a crystal organizations which can be described as stair-like, infinite one-dimensional polymers as depicted in Figure 3. In *catena*-[μ$_3$-(3,4-dimethoxybenzoato)thallium(I)] (**3**), each carboxylic group acts as a μ$_4$-bridging ligand resulting in infinite two-dimensional, puckered sheets. Finally, in *catena*-[μ$_3$-(3,5-dimethoxybenzoato)thallium(I)] (**4**) bridges each carboxylic unit three Tl$^+$ cations to form double-stranded, nearly planar, infinite array of Tl$^+$ cations, resulting in the lamellar structure shown in Figure 12. The ligands used in this study present a rather limited range of steric and electronic properties and are therefore useful for establishing basic patterns in thallium(I)−benzoate interactions. In following papers, we wish to extent these investigations where steric requirements of the ligands impose restrictions on the thallium coordination geometries and also attempt the use of the inert lone pair as a Lewis base for the construction of extended solids.

Experimental Section

Materials and Methods: Chemicals were purchased from Aldrich Chemicals and used without further purification. IR spectra were recorded with a Perkin−Elmer 1720 X FT-IR spectrometer in the 4000−400-cm^{-1} region with 2 cm^{-1} resolution both as KBr pellets and as pure powders between NaCl windows.

Preparation: All compounds were prepared by adding 5.0 mM Tl_2CO_3 to 100 mL of H_2O and 10.0 mM salicylic acid, 4-aminosalicylic acid, 3,4-dimethoxybenzoic acid or 3,5-dimethoxybenzoic acid, respectively. The solutions were allowed to boil for 2 h while stirring which in all cases yielded clear solutions. The solutions were slowly concentrated which yielded crystals of X-ray quality. The crystals chosen for X-ray analysis and the bulk material were identical as shown by superimposable IR spectra. Total yield > 90%.

***catena*-[Bis(μ$_3$-salicylato)dithallium(I)] (1):** IR: $\tilde{\nu}$ = 3065 (w), 3049 (w), 1621 (m), 1584 (w), 1564 (s), 1478 (s), 1448 (s), 1406 (w), 1384 (s), 1333 (m), 1301 (m), 1289 (w), 1251 (w), 1137 (w), 1087 (w), 1023 (w), 982 (vw), 961 (vw), 862 (s), 810 (s), 770 (s), 698 (s), 666 (s), 565 (w), 537 (w), 528 (m), 452 (w) cm^{-1}.

***catena*-[Bis(μ$_3$-*o*-aminosalicylato)dithallium(I)] (2):** IR: $\tilde{\nu}$ = 3467 (w), 3341 (w), 1619 (m), 1573 (s), 1552 (m), 1503 (s), 1444 (s), 1372 (s), 1296 (s), 964 (w), 831 (m), 782 (m), 698 (m), 626 (s), 596 (w), 531 (w), 447 (m) cm^{-1}.

***catena*-[(3,4-Dimethoxybenzoato)thallium(I)] (3):** IR: $\tilde{\nu}$ = 3083 (w), 3010 (w), 2958 (w), 2932 (w), 2901 (w), 2828 (vw), 1598 (s), 1520 (s), 1511 (m), 1460 (m), 1444 (m), 1403 (m), 1374 (s), 1354 (m), 1268 (s), 1252 (m), 1231 (s), 1180 (m), 1133 (m), 1107 (s), 1021 (s), 947 (w), 923 (w), 875 (m), 835 (m), 789 (s), 778 (s), 766 (s), 726 (w), 624 (s), 612 (w), 523 (m) cm^{-1}.

catena-[(3,5-Dimethoxybenzoato)thallium(I)] (4): IR : $\tilde{\nu}$ = 3083 (w), 3010 (w), 2958 (w), 2932 (w), 2901 (w), 2836 (w), 1598 (s), 1520(vs), 1505 (s), 1460 (w), 1444 (w), 1403 (s), 1374 (s), 1354 (w), 1268 (s),

Table 2. Crystallographic data

	1	**2**	**3**	**4**
Empirical formula	$(C_7H_5O_3Tl)_2$	$(C_7H_6NO_3Tl)_2$	$C_9H_9O_4Tl$	$C_9H_9O_4Tl$
M [g·mol^{-1}]	682.96	713.00	385.53	385.53
T [K]	295	295	295	295
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 11)	$P2_1/n$ (no. 11)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a [Å]	6.123(1)	7.039(1)	14.202(3)	19.850(3)
b [Å]	11.938(2)	11.904(2)	7.320(2)	9.793(1)
c [Å]	9.893(2)	9.463(1)	9.700(2)	10.645(1)
β [°]	93.354(4)	91.895(3)	103.427(4)	111.732(4)
V [Å^3]	721.9(2)	792.5(2)	980.8(4)	1922.2(4)
Z	2	2	4	8
Θ range [°]	2.68−25.99	2.75−26.49	3.15−28.00	2.21−28.00
Completeness to Θ_{max} (%)	99.8	95.2	96.9	97.4
μ [cm^{-1}]	22.319	20.341	16.452	16.788
Reflections measured	3894	3606	5295	5866
Unique reflections (R_{int})	1415 (0.0647)	1559 (0.0699)	2296 (0.0846)	2263 (0.0915)
Observed reflections [$I > 2\sigma(I)$]	985	955	1488	1440
R_1 (observed reflections)	0.0581	0.0627	0.0418	0.0380
wR_2 (all reflections)	0.1439	0.1487	0.0899	0.0676

1252 (w), 1231 (s), 1180 (w), 1156 (vw), 1133 (w), 1107 (s), 1033 (vw), 1021 (s), 947 (vw), 923 (vw), 875 (w), 835 (w), 789 (s), 778 (s), 766 (s), 726 (vw), 634 (s), 612 (w) cm^{-1}.

Single Crystal X-ray Crystallography: Single crystal diffraction data were collected at 298 K with a Bruker SMART platform equipped with a CCD area detector and a graphite monochromator using Mo-K_α radiation. Cell parameters were refined using 985, 955, 1488 and 1400 reflections for **1**, **2**, **3** and **4**, respectively. A hemisphere of data (1291 frames) was collected for each structure using the ω-scan method (0.3° frame width) with 40 s exposure time. The crystal−detector distance was 4.77 cm. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. Intensity decay was negligible for all compounds. Data reduction and empirical absorption correction were performed using the program packages Bruker SAINT and SADABS, respectively.[18] The structures were solved by the direct methods in SHELXTL and refined using full-matrix least-squares on F^2. Non-H atoms were treated anisotropically. Carbon-H atoms were generated in ideal positions riding on their respective carbon atom. Oxygen-H and nitrogen-H atoms were localized on difference Fourier maps but their distances were constrained to 0.82 and 0.86 Å, respectively. Crystal and experimental data are summarized in Table 2. CCDC-174558 (**1**), -174556 (**2**), -174555 (**3**) and -174557 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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