

Complexity of Coordinative Bonding in Thallium(I) Anthranilates and Salicylates

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Abstract: An inventory of the structural chemistry of thallium(I) shows many unexpected, almost random coordination numbers and coordination geometries that appear erratic and inconsistent. This nonstandard behavior is often ascribed to the specific lone-pair characteristics originating from relativistic effects. To provide data on a set of closely related compounds from which simple general rules of coordinative bonding at Tl^+ can be established, three thallium(I) anthranilates and three thallium(I) salicylates have been prepared from Tl_2CO_3 and the corresponding 2-amino- and 2-hydroxy-benzoic acids and crystallized from aqueous solutions. All six compounds, the simple anthranilate (**1**) and salicylate (**4**) and the 3- and 4-methyl-substituted homologues (**2**, **3** and **5**, **6**) show different structures with large variations in the coordination motif. The coordination by oxygen in a geometry which covers less than a coordination hemisphere is the only common feature, complemented (only in **1**) by a nitrogen coordination and by η^6 -coordination of one (in **1**, **2**, **3**, **6**) or two phenyl rings (in **4**). $Tl-Tl$ contacts for which "thallophilic" bonding between closed shell metal atoms could be invoked, are generally very long (close to 4.0 Å) or even well beyond the limit of standard van der Waals contacts. Hydrogen bonding is only obvious for the internal contacts of the amino- or hydroxy-benzoate ligands and does not contribute significantly to the assembly of the supramolecular structure which is dominated by oxygen bridges between thallium atoms. With the exception of **5**, the formula units $Tl[O_2C(2-R)(3-R')(4-R'')C_6H_2]$ are generally aggregated into dimers of various configurations depending on the relative orientation of the edge-sharing four-membered rings, and these dimers are further linked into strings or columns establishing $N-Tl$ or $Tl-O$ contacts and arene coordination. The drastic changes induced in the structures upon only small variations such as methyl substitution in 3- or 4-position of the ligand suggest that thallium(I) coordination is generally restricted to one hemisphere of nearest neighbors, but is extremely flexible in this realm. The open hemisphere may be partially capped by arene coordination (which is weak at a distance of ca. 3.1 Å to the centroid of the ring) or feature very weak thallophilic contacts.

Introduction

In modern coordination chemistry the role of most metals as clustering centers for ligands appears to be predictable. From a consideration of the size and the electronic configuration in a certain oxidation state of the acceptor center, and of the relative size and donor properties of the ligand functions, the coordination number and the coordination geometry can be extrapolated for most of the common metal/ligand combinations with quite high certainty. Although this is generally true, the situation is surprisingly difficult for main group metals in their low oxidation states in which they are to be assigned lone pairs of electrons.

A prominent example for pertinent complications is *thallium(I)* with its bewildering complexity of coordination numbers and geometries.¹ Although one of the larger cations, with tabulated ionic radii between 1.45 and 1.59 Å (intermediate between those of potassium and rubidium),² it often shows

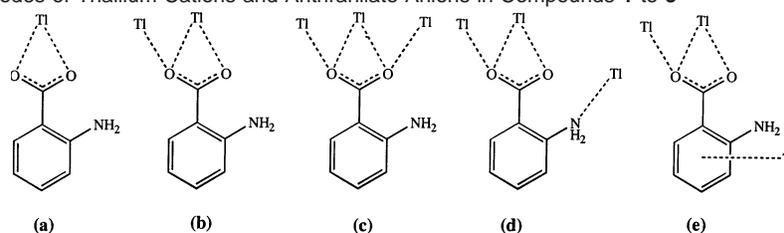
exceedingly low coordination numbers in geometries which leave a large part of the coordination sphere seemingly unoccupied.³ By contrast, potassium and rubidium cations always have their coordination sphere covered as completely and as symmetrically as possible, optimizing the Coulomb energy.

Thallium(I) coordination may be generally built on several quite different types of metal–ligand interactions: Owing to the relativistically contracted valence shell and the low electrical charge, the Tl^+ cation is intermediate between standard hard and soft character and has affinity for both hard and soft donor atoms, like oxygen and sulfur, or chloride and iodide, and so forth. Therefore, there is a plethora of very stable hydroxide, alkoxide, and carboxylate, but also sulfide, thiolate, thiocarboxylate, or thiocarbamate complexes, with $Tl-O$ and $Tl-S$ coordination, respectively.¹ However, these ligands cover only a certain part of the environment even if ligands are available in large excess. Attempts to ascribe this phenomenon solely to the stereochemically active $6s^2$ lone pair of electrons have not

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Scheme 1: Coordination Modes of Thallium Cations and Anthranilate Anions in Compounds 1 to 3

been fully convincing in quite a number of cases with nonstandard coordination geometries.⁴

In the resulting bare regions the coordinated $[Tl]^+$ ion often has very distant contacts (up to 4.0 Å) with $[Tl]^+$ centers of neighboring complexes, but the significance of this type of interaction—if there is any—has recently been the subject of much debate.^{5–23} “Thalophilic” Tl–Tl contacts should probably be considered as particularly weak cases of “metallophilic” bonding⁵ between closed-shell atoms as compared for example to the particularly strong “aurophilic” bonding between Au^+ complexes.^{24–26} Notwithstanding, relativistic and correlation effects which are known to affect most strongly the energy of the $6s^2$ electrons of the heaviest metals in the last period and thus to determine the energy levels of the frontier orbitals,²⁷ are also held responsible for the unusual properties of mixed-metal complexes where the two extreme cases, Tl^+ and Au^+ , are combined, in which short contacts are indicative of strong closed-shell interactions.^{5,28,29}

In the ligand-bare regions of its coordination sphere, Tl^+ —unexpected for a main group metal—also forms π -complexes with aromatic hydrocarbons as first demonstrated for the anionic cyclopentadienyl ligands^{30,31} in 1957, and in 1985 for neutral arenes.^{32,33} In these compounds the cation has a centered η^6 -coordination at rather large metal-centroid distances of ca. 3.05 Å. Recently, investigations of the complexation modes of monovalent thallium ions were extended to the tris- and poly-(pyrazolyl)borate as well as the tris(indazolyl)borate ligands.³⁴ The crystalline phases of these compounds reveal many variations in the metal–ligand arrangement and crystal packing: In addition to the complexation of the thallium ions by the nitrogen donors and arene moieties, Tl–Tl-interactions and π – π -stacking are also observed. A series of 3,5-disubstituted pyrazolates shows analogous complexation modes.³⁵

In the present study, the structural chemistry of thallium(I) anthranilates and salicylates with a selected substitution pattern was investigated with the following incentives (Scheme 1):

(1) Anthranilate and salicylate anions offer hard and strongly basic donor centers in a ligand geometry facilitating chelation and/or metal bridging for a medium- to large-size cation and should be prone to fill its coordination sphere exhaustively. (2) If bare regions are left in the coordination sphere despite the over-supply of ligand donor functions, then the ligands would still be capable to cover these regions by arene coordination. (3) If a given substitution pattern of the ligands will rule out such η^6 -arene interactions due to steric hindrance, then the monomeric or oligomeric units may aggregate via thalophilic contacts. (4) Both the hydroxy and the amino group in salicylate or anthranilate anions, respectively, can entertain intra- and/or intermolecular hydrogen bonding to assist a multidimensional assembly of the components.

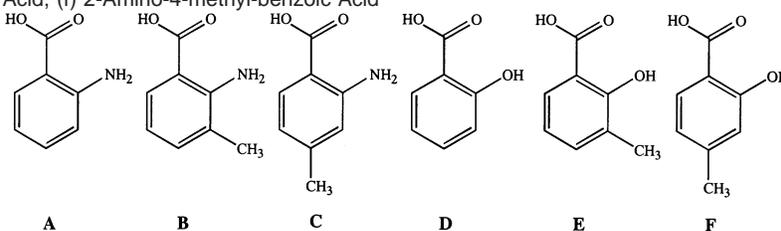
From the evaluation of the structural chemistry of compounds with a set of closely related ligands the interplay between the various bonding contributions may become obvious and help to understand the complexity of the systems.

Work described in a recent publication by Kristiansson⁴ followed similar lines and reached similar conclusions for three thallium benzoates including salicylate $Tl^+(2-HO-C_6H_4-$

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Scheme 2: Benzoic Acids Chosen for the Structural Investigation of Their Thallium(I) Salts. (a) 2-Amino-benzoic Acid (anthranilic acid), (b) 2-Amino-3-methyl-benzoic Acid, (c) 2-Amino-4-methyl-benzoic Acid, (d) 2-Hydroxy-benzoic Acid (salicylic acid), (e) 2-Hydroxy-3-methyl-benzoic Acid, (f) 2-Amino-4-methyl-benzoic Acid

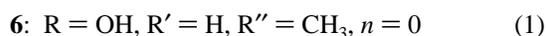
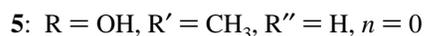
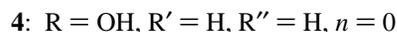
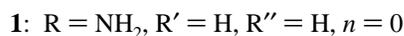
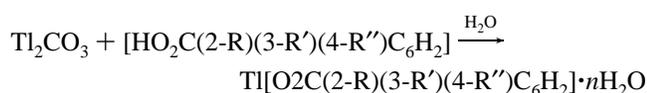


(COO)⁻. This work was preceded by a structural study of thallium(I) 3-hydroxy-benzoate³⁶ and by a brief investigation of the solution chemistry of thallium(I) salicylate.³⁷ Our own study is an extension of recent investigations of the anthranilates and salicylates of other main group metals, mainly Li, Be, Na, Mg, K, and Ca, where the absence of lone pairs of electrons and the insignificance of relativistic effects leads to conventional modes of coordinative bonding.^{38–40} It is particularly noteworthy that in crystals of *potassium* anthranilate the cations are completely shielded by oxygen donor atoms and reach coordination number 7.

Thallium(I) coordination was already probed in this laboratory recently with amino acids and related biorelevant ligands,⁴¹ and arene coordination to Tl⁺ was the subject of earlier investigations.⁴²

Preparations

The thallium(I) salicylates and anthranilates can be prepared by neutralization of thallium(I) carbonate with the corresponding acid in boiling water. After reflux for 30 min, clear solutions are obtained from which the products crystallize on cooling in almost quantitative yields (82–96%). Single crystals can be grown by slow recrystallization of pure samples. Elemental analyses and crystal structure determinations have shown that all products except one are anhydrous. Equation 1 and Scheme 2 illustrate the set of hydroxy- and amino-benzoates employed in the preparative and structural studies



The compounds are colorless to pale yellow crystalline materials which are stable in air and not hygroscopic. Data of elemental analyses, and lists of characteristic IR-absorption bands (in KBr) and of prominent peaks in the mass spectra (chemical ionization)

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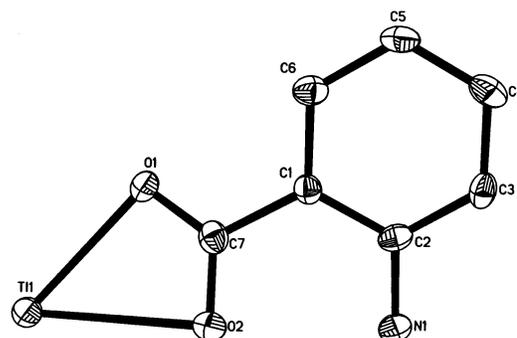


Figure 1. Asymmetric unit in the structure of C₇H₆NO₂Tl, **1** (ORTEP drawing with 50% probability ellipsoids and atomic numbering).

are given in the Experimental section. These data are not discussed here any further because of their low diagnostic value.

Crystal Structures

In the discussion of the individual structures of the six thallium anthranilates and salicylates the simple (unsubstituted) anthranilate will be given a detailed consideration because it features all important types of thallium coordination. The substituted anthranilates and the corresponding salicylates will be treated less comprehensively, only pointing out the significant differences caused by the introduction of methyl groups at various positions of the amino- or hydroxy-benzoate ligands.

Thallium(I) 2-amino-benzoate (anthranilate, **1).** Crystals of Tl⁺[C₇H₆NO₂]⁻ are orthorhombic, space group *Pbca*, with *Z* = 8 formula units in the unit cell. The asymmetric unit contains only one formula unit (Figure 1). The carboxylate group is chelating the metal atom with two significantly different metal–oxygen contacts of Tl1–O1 2.554(4) and Tl1–O2 2.774(5) Å. The four-membered ring is wedge-like with an angle O1–Tl1–O2 of only 48.97(11)°, and the two oxygen atoms thus cover only a very small fraction of the coordination sphere of the metal atom.

These monomers dimerize via donor–acceptor interactions between O1 and Tl1 of neighboring units to give a four-membered ring Tl1–O1–Tl1A–O1A as shown in Figure 2. The angle O1–Tl1–O1A is again small at 74.73(13)° and the additional contact Tl1–O1A is 2.717(4) Å long. The two wedges and the four-membered ring are almost coplanar keeping O1, O1A, and O2 at a given thallium atom in quasi-meridional positions.

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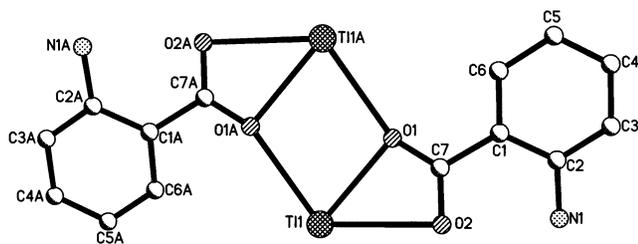


Figure 2. Dimerization of the formula unit in the crystalline phase of compound **1**. The resulting four-membered ring $\text{Tl}(1)_2\text{O}(1)_2$ is planar.

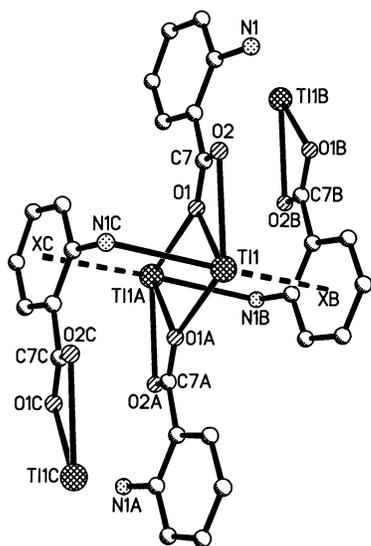


Figure 3. In the crystal structure of compound **1**, dimers are shifted relative to each other in order to establish Tl –(arene) and Tl – N contacts between neighboring formula units. Note that an inversion center is situated in the focal point of the $\text{Tl}(1)_2\text{O}(1)_2$ -rhomboid. Selected bond lengths [Å], angles [°] and symmetry transformations: $\text{Tl}(1)$ – $\text{O}(1)$ 2.554(4), $\text{Tl}(1)$ – $\text{O}(2)$ 2.774(5), $\text{Tl}(1)$ – $\text{O}(1\text{A})^1$ 2.717(4), $\text{Tl}(1)$ – $\text{N}(1\text{C})^2$ 2.838(5), $\text{Tl}(1)$ – XB^3 (centroid) 3.372(6); $\text{O}(1)$ – $\text{Tl}(1)$ – $\text{O}(1\text{A})^1$ 74.73(13), $\text{O}(1)$ – $\text{Tl}(1)$ – $\text{O}(2)$ 48.97(11), $\text{O}(1\text{A})^1$ – $\text{Tl}(1)$ – $\text{O}(2)$ 122.51(11), $\text{Tl}(1)$ – $\text{O}(1)$ – $\text{Tl}(1\text{A})^1$ 105.27(13); $^1 -x, -y, -z + 1$; $^2 x, y - 1, z$; $^3 -x, -y + 1, -z + 1$.

This oxygen donor atom distribution still means very poor (meridional) shielding of the metal atom.

Through stacking of the flat dimers each thallium atom builds contacts with an amino group on one side and an η^6 arene ring on the other (Figure 3). Through these external contacts the dimers are aggregated into strings of dimers. The distance Tl1 – N1C [2.838(5) Å] is only slightly longer than the Tl – O distances indicating comparable strengths of this dative bond. On the opposite side of the flat dimer the metal atom is almost centrally located above the benzene ring with a Tl1 – XB (centroid) distance of 3.372(6) Å. This distance is about 10% larger than the reference value reported for a mesitylene ring at Tl^+ in $[(\text{C}_6\text{H}_3\text{Me}_3)_3\text{Tl}_2(\text{GaBr}_4)_2]_2$, which is not unexpected because mesitylene is a much better donor than amino-benzoate, and Tl^+ must be a much stronger acceptor in its tetrabromogallate salt as compared to the anthranilate.

These additional contacts complement a coordination hemisphere which still leaves the metal atom wide open in its second hemisphere: At the rim of the filled hemisphere the angles O2 – Tl1 – O1A [122.51(11)°] and N1C – Tl1 – XB [148.08(14)°] are both much less than 180°. The vacancy appears to be finally compensated by inter-string contacts between thallium atoms (Figure 4): Through the packing of the strings of dimers each

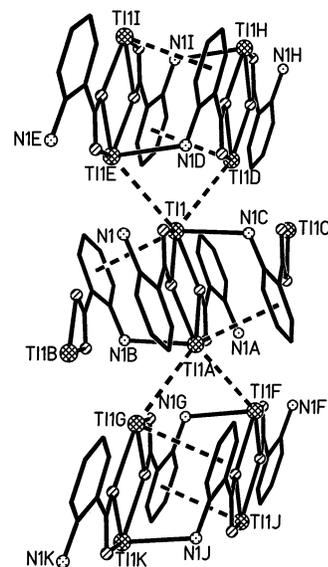


Figure 4. Excerpt from the cell plot of the crystalline phase of compound **1**, illustrating the long metallophilic contacts between $[\text{Tl}]^+$ cations of adjacent columns of dimers.

thallium atom acquires two nearest thallium neighbors at a distance of Tl1 – Tl1D 3.967(6) Å. This value is in good agreement with data published for a group of thallium(I) complexes where association can be assumed in the solid state via thalophilic interactions.^{4–23} However weak the thalophilic contacts may be, the orientation of the metal atoms at the periphery of the columns suggests that there should be some contribution to the overall stability of the solid-state structure. All other Tl – Tl contacts (within a dimer or between dimers of the same string) are well beyond 4.0 Å.

Hydrogen bonds have not been localized owing to the uncertainties associated with the positions of the N -bound hydrogen atoms. From the diagrams it appears that there may be a significant internal hydrogen bonding in each amino-benzoate group between O2 as an acceptor and N1 – H as a donor (Figure 1). This hydrogen bond is also suggested by similar findings for the salicylate (ref 4 and below). There are no other discernible N – H – O connectivities.

Thallium(I) 2-amino-3-methyl-benzoate (3-methyl-anthranilate, 2). Crystals of $\text{Tl}^+[\text{C}_8\text{H}_8\text{NO}_2]^-$ are monoclinic, space group $C2/c$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains one formula unit. As described for **1** (above) the anion is chelating the metal atom to form a wedge-like four-membered ring. These fundamental units aggregate to give dimers the atoms of which are related by a center of inversion in the middle of the central rhombus (Figure 5). The dimensions of these quasi-planar dimers are very similar to those in **1**. The geometry also suggests intramolecular hydrogen bonding between the atoms O2 and N1 , although the hydrogen atoms have not been definitely located.

While the dimers of the anthranilate **1** are joined into strings via Tl – N and Tl –(arene) coordination (Figure 3), the aggregation of the 3-methyl-anthranilate **2** is established via a bridging function of the carboxylate oxygen atoms O2 (Figure 6). In contrast to the planar rhombus Tl1 – O1 – Tl1A – O1A found in the dimer, the four-membered rings Tl1 – O2 – Tl1A – O2A are folded into a butterfly shape with a folding angle of 88.67(19)°. The backbone of a string of dimers is therefore a sequence

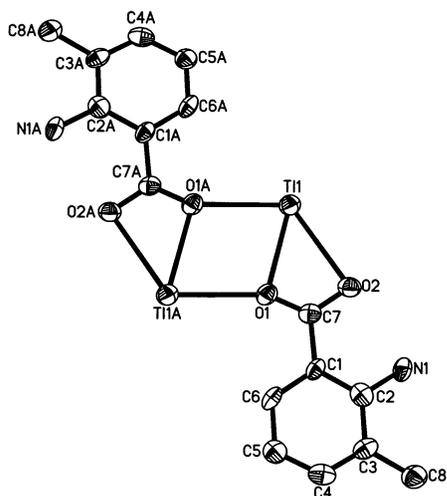


Figure 5. Dimerization in the crystalline phase of $C_8H_8NO_2Tl$, **2** (ORTEP drawing with 50% probability ellipsoids and atomic numbering).

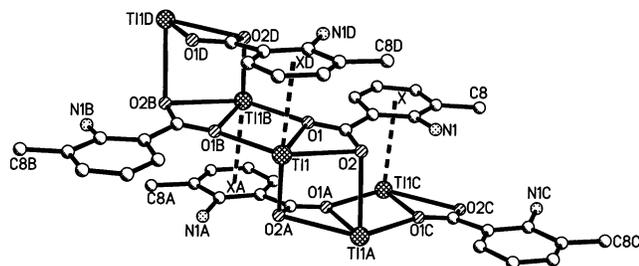


Figure 6. Aggregation of dimers in the crystal structure of **2** resulting in the formation of stair-like chains. The thallium atoms are partially shielded through Tl–(arene) contacts. Selected bond lengths [Å], angles [°] and symmetry transformations: Tl(1)–O(1) 2.572(7), Tl(1)–O(2) 2.779(7), Tl(1)–O(1B)¹ 2.676(7), Tl(1)–O(2A)² 2.757(7), Tl–XD³(centroid) 3.230(10); O(1)–Tl(1)–O(1B)¹ 73.9(2), O(1)–Tl(1)–O(2A)² 73.7(2), O(1B)¹–Tl(1)–O(2A)² 80.1(2), O(1)–Tl(1)–O(2) 49.0(2), O(1B)¹–Tl(1)–O(2) 122.4(2), O(2A)²–Tl(1)–O(2) 77.5(2), Tl(1)–O(1)–Tl(1B)¹ 106.1(2); ¹ $-x, -y, -z$; ² $-x, y, -z - 1/2$; ³ $x, -y, z + 1/2$.

of four-membered rings (Tl_2O_2) and ($TlCO_2$) in the forms of a wedge, a flat rhombus and a folded rhombus. Complexation of the metal atom through four oxygen atoms in a small quadrant of the coordination sphere is supplemented by a weak Tl–(arene) contact (Tl1–XD (centroid) 3.230(11) Å). Contrary to the situation in **1** the nitrogen atoms of compound **2** are not coordinated to the thallium atoms [Tl1–N1 4.157(15) Å].

Along each string the almost perfectly planar dimeric units shown in Figure 5 are arranged parallel as indicated by the sidewise projection shown in Figure 6, but there is no phenyl stacking. An alternative projection along the columns in the unit cell shows that there are no conspicuous contacts between neighboring amino-methyl-benzoate ligands. However, the thallium atoms have become located on two opposite sides of each column and are directly exposed to the thallium atoms of the neighboring columns (Figure 7). The contacts between neighboring zigzag chains of metal atoms [4.054(14) Å] are longer than in **1** and make it doubtful that there are any significant bonding contributions at these distances. This arrangement leaves the metal atoms with an extreme undersupply of ligand donor atoms.

Thallium(I) 2-amino-4-methyl-benzoate (4-methyl-anthranilate semihydrate, 3). Crystals of compound **3** are monoclinic, space group $C2/c$, with $Z = 16$ formula units in the unit cell

(Figure 8). The asymmetric unit contains two independent formula units. In only one of these two units the metal cation (Tl1) is chelated by its anthranilate anion, whereas the other (Tl2) is bridged by the anion to give an eight-membered ring as the central unit of a tetramer (Figure 9). The peripheral wedges are attached to the central eight-membered ring via butterfly-type folded four-membered rings. Both Tl1 and Tl2 are further η^6 -coordinated to the phenyl rings of neighboring tetramers with Tl1–X1B (centroid) and Tl2–X2B (centroid) distances of 3.166(13) and 3.181(15) Å as illustrated in Figure 9. The Tl1–Tl2 and Tl1–Tl2A contacts within a tetramer have distances just below 4.0 Å, but the corresponding Tl1–O–Tl2 angles are very sharp, suggesting that there is no significant thalophilic bonding. There are also no Tl–N contacts. Both Tl1 and Tl2 are thus tri-coordinated by nearest oxygen atoms in steep trigonal pyramids and η^6 -capped by one arene group.

As already proposed for compounds **1** and **2**, hydrogen bonding is expected to exist between N1 and O12 and N2 and O22. The water molecules (O01, O01A) appear in symmetry-related pairs between the strings of complexes near the atoms O11 and N2 and are most certainly linked there via hydrogen bonds (Figure 10), but no refinement of the hydrogen positions was possible from the data set collected for this structure with its many heavy atoms.

Thallium(I) 2-hydroxy-benzoate (salicylate, 4). The crystal structure of compound **4** has also been determined very recently and independently by Kristiansson as part of a study on complexes of monovalent thallium ions with functionalized benzoate ligands.⁴ Our results are in full agreement with the published data. To summarize, two formula units appear as dimers similar to those of the anthranilate **1**, but the aggregation of these flat dimers into strings (cf. Figures 2, 3) leads to *two* η^6 -coordinated arene units at each thallium atom. In addition, a hydroxy group of a neighboring salicylate unit has a close contact with a given metal atom which resembles the N–Tl contact of an anthranilate unit in complex **1**. The Tl⁺ cations in the salicylate **4** are therefore the most shielded metal atoms of the whole series (4 oxygen donors and two phenyl rings). No Tl–Tl contacts are discernible.

Thallium(I) 2-hydroxy-3-methyl-benzoate (3-methyl-salicylate, 5). Crystals of compound **5** are triclinic, space group $P\bar{1}$, with two formula units in the unit cell. The monomeric unit features a benzoate-chelated thallium atom and a hydrogen bond between the hydroxy group and one of the carboxylate oxygen atoms. These monomers are arranged in stacks with Tl1–Tl1A contacts of 3.921 Å and all Tl atoms on a straight line which is tilted against the planes of the monomers by about 65° (Figure 11). These geometrical parameters make significant thalophilic bonding very unlikely.

Neighboring stacks of this type are indented meaning that neighboring monomers of different stacks are not on the same level but shifted to make the distances of a given Tl atom to two monomers of the second stack about equal: Tl1–O1C 2.882(5), Tl1–O1D 2.902(5) Å. It is therefore not justified to take any two monomers of different stacks as an independent dimer similar to those selected in all four previous structures (**1–4**). In the double-stacks each thallium atom is provided with *two* additional oxygen atoms (O1C and O1D for Tl1) making it four-coordinated (Figure 11), whereas in the previous structures there was only one closely neighboring unit in the

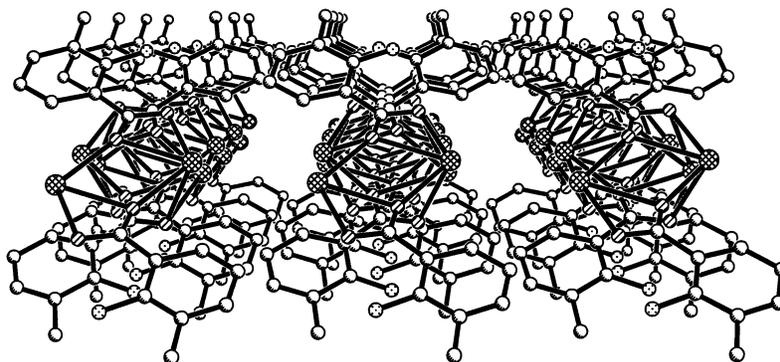


Figure 7. Cell plot of the crystalline phase of **2**. In contrast to **1**, no metalphilic interactions between adjacent strings are observed.

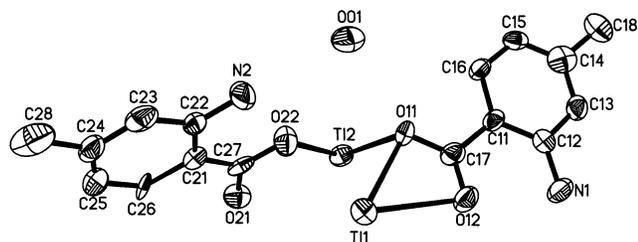


Figure 8. Asymmetric unit in the structure of $C_8H_9NO_{2.5}Tl$, **3**, with atomic numbering (ORTEP drawing with 50% probability ellipsoids).

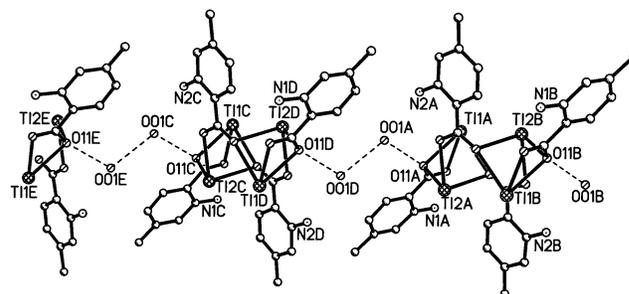


Figure 10. Pairs of symmetry-related water molecules are located in the voids between the tetramers in **3**, most probably stabilizing the crystalline phase through a set of hydrogen bonds.

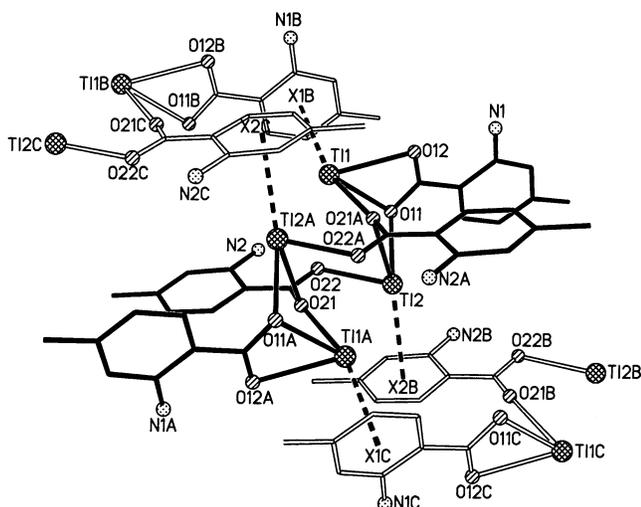


Figure 9. In the crystal structure of **3**, four-membered Tl_2O_2 -rings are fused to eight-membered $Tl_2C_2O_4$ -rings. Neighboring formula units offer their benzene rings for Tl -(arene) complexation. Selected bond lengths [Å], angles [°] and symmetry transformations: $Tl(1)-O(11)$ 2.601(11), $Tl(1)-O(12)$ 2.719(11), $Tl(1)-O(21A)^1$ 2.793(11), $Tl(1)-X1B^2$ (centroid) 3.166(13), $Tl(2)-O(22)$ 2.509(12), $Tl(2)-O(11)$ 2.711(10), $Tl(2)-O(21A)^1$ 2.784(11), $Tl(2)-X2B^3$ (centroid) 3.181(15); $O(11)-Tl(1)-O(12)$ 49.3(3); $O(11)-Tl(1)-O(21A)^1$ 79.2(3), $O(12)-Tl(1)-O(21A)^1$ 74.7(3), $O(22)-Tl(2)-O(11)$ 69.0(3), $O(22)-Tl(2)-O(21A)^1$ 83.5(4), $O(11)-Tl(2)-O(21A)^1$ 77.5(3), $Tl(1)-O(11)-Tl(2)$ 94.2(3), $Tl(2A)^1-O(21)-Tl(1A)^1$ 88.5(3); $^1 -x + 1/2, -y - 1/2, -z + 1$; $^2 x, y - 1, z$; $^3 x, y + 1, z$.

adjacent stack providing only one oxygen donor atom and making the thallium atom three-coordinated (see e.g., Figure 2).

Neighboring double-stacks of monomers are packed in such a way that each hydroxy-substituent can function as an additional donor [$Tl-O3E$ 2.976(5) Å] which finally rises the coordination number of each thallium atom (solely with oxygen atoms) to five (Figure 11). This set of five oxygen atoms covers just about one hemisphere of the thallium environment and no other

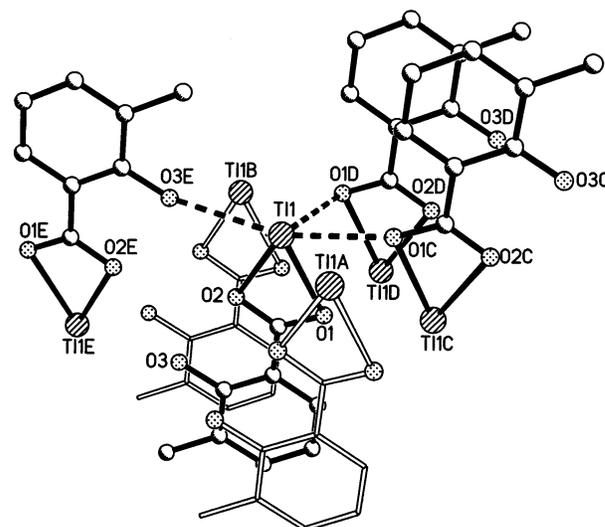


Figure 11. Alignment of adjacent formula units in the crystalline phase of **5** is not determined by Tl -(arene) or $Tl-Tl$ contacts, but by $Tl-O$ interactions instead. Note that each O1 oxygen atom has contact with three thallium ions. Selected bond lengths [Å], angles [°] and symmetry transformations: $Tl(1)-O(1)$ 2.734(6), $Tl(1)-O(2)$ 2.749(5), $Tl(1)-O(1C)^1$ 2.882(5), $Tl(1)-O(1D)^2$ 2.902(5), $Tl(1)-O(3E)^3$ 2.976(5); $O(1)-Tl(1)-O(2)$ 48.03(14), $O(1)-Tl(1)-O(1C)^1$ 85.88(17), $O(2)-Tl(1)-O(1C)^1$ 85.88(17), $O(1)-Tl(1)-O(1D)^2$ 65.85(18), $O(2)-Tl(1)-O(1D)^2$ 80.19(16), $O(1C)^1-Tl(1)-O(1D)^2$ 85.29(13), $O(1)-Tl(1)-O(3E)^3$ 111.75(15), $O(2)-Tl(1)-O(3E)^3$ 64.59(15), $O(1C)^1-Tl(1)-O(3E)^3$ 161.45(15), $O(1D)^2-Tl(1)-O(3E)^3$ 96.49(15); $^1 -x, -y + 2, -z + 2$; $^2 -x + 1, -y + 2, -z + 2$; $^3 -x + 1, -y + 1, -z + 2$.

contacts are discernible in the other half of the coordination sphere.

Introduction of the methyl group in the 3-position of the salicylate ligand is thus found to induce an aggregation of the monomers in a new motif with the thallium cation solely

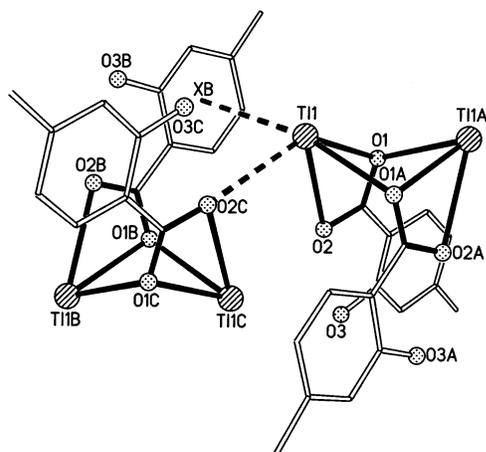


Figure 12. Aggregation of the dimers (in the crystalline phase of **6** allows for arene as well as for weak oxygen contacts which determine the mutual positioning. Selected bond lengths [Å], angles [°] and symmetry transformations: Tl(1)–O(1) 2.626(4), Tl(1)–O(2) 2.764(4), Tl(1)–O(1A)¹ 2.778(4), Tl(1)–O(2C)² 3.158(4), Tl–XB³(centroid) 3.304(8); O(1)–Tl(1)–O(2) 48.52(11), O(1)–Tl(1)–O(1A)¹ 72.53(14), O(2)–Tl(1)–O(1A)¹ 73.02(11), O(1)–Tl(1)–O(2C)² 137.05(10), O(2)–Tl(1)–O(2C)² 88.75(10), O(1A)¹–Tl(1)–O(2C)² 93.31(10), Tl(1)–O(1)–Tl(1A)¹ 93.18(12); ¹ $-x, y, -z + 3/2$; ² $-x, -y, -z + 1$; ³ $x, -y, z - 1/2$.

coordinated with oxygen atoms of four different 2-hydroxy-3-methyl-benzoate ligands.

Thallium(I) 2-amino-4-methyl-benzoate (4-methyl-salicylate, 6). Crystals of compound **6** are monoclinic, space group $C2/c$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains only one monomer with a structure closely related to that of **4** and **5**. These monomers form a new type of dimer, where two edges Tl1–O1/Tl1A–O1A form a butterfly-type four-membered ring with the wedge-type four-membered rings folded to the same side on opposite edges of the butterfly (Figure 12). This dimer has 2-fold symmetry with the C_2 axis passing through the middle of the Tl1–Tl1A folding edge.

Each thallium atom of a dimer has an oxygen atom O2 at a rather distant contact [Tl1–O2C 3.158(4) Å] from a neighboring dimer and is η^6 -coordinated to one phenyl ring of the same ligand [Tl–XB (centroid) 3.304(8) Å]. Within one hemisphere, the thallium atoms thus have three near and one more distant oxygen neighbors and are further shielded by one benzene ring (Figure 12). All Tl–Tl contacts are longer than 4.0 Å.

Introduction of a methyl group in the 4-position instead of the 3-position of the salicylate ligand (**6** vs **5**) causes again a new packing pattern for the same monomeric units with strongly reduced oxygen coordination (from 5 to 3 + 1) at the thallium atom, but a return to π -complexation previously found in the substituent-free salicylate (**4**).

Conclusions

The structures of compounds **1** to **6** show the following common features: (1) All formula units have the metal atom chelated by the carboxylate group of the amino-/hydroxy-benzoate ligand to give a wedge-like four-membered ring. (Only Tl2 in compound **3** is not chelated, but has the ligand as a bridge to a neighboring metal atom.) (2) These monomers form dimers by establishing mutual Tl–O coordination generating rhomboid four-membered rings. These dimers may be flat (**1**, **2**, **4**) or highly folded (**3**, **6**). (Only compound **5** is an exception, where no discrete dimers are discernible and aggregation occurs in

Tl–O–Tl–O zigzag chains between double-stacks of monomers.) (3) Donor substituents may be employed as ligands ($-\text{NH}_2$ in **1**, but not in **2** and **3**; $-\text{OH}$ in **4** and **5**, but not in **6**). (4) η^6 -Arene coordination contributes to the shielding of the metal atoms in most cases (**1**, **2**, **3**, **4** and **6**), but is absent for the 2-amino-3-methyl-benzoate ligand (**5**). (5) There is no discernible π – π -stacking or $\text{C–H}\cdots\pi$ -embracing of the arene moieties.⁴³ (6) Hydrogen bonding of the $-\text{NH}_2$ / $-\text{OH}$ groups is only obvious for internal interactions of the ligand in each monomer and plays no role in determining the supramolecular assembly of the monomers. (7) All Tl–Tl contacts are very long and thalophilic bonding seems to play no or only a very minor role in determining the crystal structures.

From the above observations, it may be concluded that the bonding of the ligands to the metal should be taken as largely ionic which can explain the flexibility of the coordination number and coordination geometry and the clear preference for the hard oxygen atoms of the carboxylate group. This result is in excellent agreement with recent solution studies using large-angle X-ray scattering and EXAFS techniques.⁴⁴

The attachment of the ligands in only one hemisphere of the ligand environment indicates the role of the $6s^2$ lone pair of electrons which is highly contracted by relativistic effects.^{5,27} Capping of parts of the coordination sphere by arene coordination³³ at distances larger than 3.0 Å or through long Tl–Tl contacts with distances near the sum of the van der Waals radii of ca. 3.92 Å appear to contribute very little to the overall stability of the aggregates as witnessed by the almost random presence or absence of such interactions depending on only small changes in the substituent pattern.⁴⁵

Finally, it should be remembered that in the analogous *potassium* anthranilate⁴⁰ the metal cations—with an ionic radius not much smaller than that of thallium—are completely surrounded by oxygen donor atoms reaching coordination number 7. This comparison perhaps reflects best the effects of a relativistically contracted $6s^2$ lone pair of electrons for the most heavy elements of the Periodic Table. It is very tempting to assume that the toxicity of thallium salts may be associated with the pronounced asymmetry of coordination which is the most obvious distinction from the symmetrical coordination of alkali metals. However, other factors such as the affinity to sulfur also contribute to the specific physiological effects of the heaviest main group metals in the Periodic Table (Hg, Tl, Pb, and Bi).

Experimental Section

All experiments were carried out in pure water. All reagents were commercially available. Standard equipment was used throughout.

Thallium(I) 2-Amino-benzoate, 1. Anthranilic acid (0.436 g, 3.2 mmol) is dissolved in 20 mL of boiling water and Ti_2CO_3 (0.75 g, 1.6 mmol) is added with stirring. The reaction mixture is refluxed for 30 min and subsequently cooled to room temperature. The product crystallizes in long, yellow, transparent needles; Yield 1.00 g (91%). Calcd. for $\text{C}_7\text{H}_6\text{NO}_2\text{Ti}$: C 24.69, H 1.78, N 4.13, Ti 60.00, O 9.40; Found: C 24.66, H 1.79, N 4.23, Ti, 60.40, O 8.92% (from the difference to 100%). IR (KBr, cm^{-1}): 3427, s, $\nu(\text{O–H})$; 3321, s, $\nu_{\text{asym}}(\text{N–H})$; 3028, m, $\nu_{\text{sym}}(\text{N–H})$; 1608, s, $\nu_{\text{asym}}(\text{C–O})$, $\delta(\text{N–H})$; 1577, s, $\nu(\text{C=C})$; 1526, s, $\nu(\text{C=C})$; 1441, s, $\nu(\text{C=C})$; 1376, s, $\nu_{\text{sym}}(\text{C–O})$; 1316, s, $\nu(\text{C–N})$; 1249, s, $\delta(\text{C–H})$; 1157, s, $\delta(\text{C–H})$; 1028, w, $\delta(\text{C–H})$; 862, m, $\gamma(\text{C–H})$; 806, m, $\gamma(\text{C–H})$; 748, m, $\gamma(\text{C–H})$; 662,

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Table 1. Crystal Data, Data Collection, and Structure Refinement of Compounds **1** to **3**, **5**, and **6**

	Thallium(I) 2-amino- benzoate, 1	Thallium(I) 2-amino- 3-methyl- benzoate, 2	Thallium(I) 2-amino- 4-methyl- benzoate hemihydrate, 3	Thallium(I) 2-hydroxy- 3-methyl- benzoate, 5	Thallium(I) 2-hydroxy- 4-methyl- benzoate, 6
crystal data					
formula	C ₇ H ₆ N ₁ O ₂ Tl ₁	C ₈ H ₈ N ₁ O ₂ Tl ₁	C ₈ H ₉ N ₁ O _{2.5} Tl ₁	C ₈ H ₇ O ₃ Tl ₁	C ₈ H ₇ O ₃ Tl ₁
<i>M_r</i>	340.50	354.52	363.53	355.51	355.51
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>Pbca</i>	<i>C2/c</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>C2/c</i>
<i>a</i> (Å)	13.5580(3)	21.8600(16)	23.0796(8)	3.9183(2)	20.1767(10)
<i>b</i> (Å)	5.9210(1)	7.8832(7)	6.9008(2)	7.9082(4)	7.3226(4)
<i>c</i> (Å)	18.1520(5)	9.7819(8)	23.5642(10)	13.8470(9)	11.4156(6)
α (°)	90	90	90	95.824(2)	90
β (°)	90	101.012(5)	101.099(1)	91.555(2)	103.584(3)
γ (°)	90	90	90	104.296(4)	90
<i>V</i> (Å ³)	1457.19(6)	1654.6(2)	3682.8(2)	413.03(4)	1639.43(15)
ρ_{calc} (g cm ⁻³)	3.104	2.846	2.623	2.859	2.881
<i>Z</i>	8	8	16	2	8
F(000)	1216	1280	2640	320	1280
μ (Mo K α) (cm ⁻¹)	22.108	19.476	17.508	19.511	19.662
data collection					
measured refl.	21375	12816	26006	15474	34951
unique refl.	1551 [<i>R</i> _{int} = 0.064]	1829 [<i>R</i> _{int} = 0.079]	3972 [<i>R</i> _{int} = 0.071]	1697 [<i>R</i> _{int} = 0.055]	1814 [<i>R</i> _{int} = 0.069]
abs. correction					
<i>T</i> _{min} / <i>T</i> _{max}	0.166/0.638	0.326/0.755	0.402/0.796	0.271/0.721	0.247/0.705
refinement					
ref. parameters	100	109	226	109	109
final <i>R</i> values [<i>I</i> ≥ 2 σ (<i>I</i>)]					
<i>R</i> 1 ^a	0.0278	0.0480	0.0614	0.0329	0.0355
<i>wR</i> 2 ^b	0.0739	0.0936	0.1398	0.0857	0.0959

^a *R*1 = $\sum(|F_o| - |F_c|)/\sum|F_o|$. ^b *wR*2 = $\{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a, b: free variables. For data of **4**, See ref 4.

s, γ (N–H); 530, m, ν (CO₂). MS (CI); L = deprotonated ligand: *m/z* = 547, [²⁰⁵TiL + ²⁰⁵Ti]⁺; 545 [²⁰⁵TiL + ²⁰³Ti]⁺; 543 [²⁰³TiL + ²⁰³Ti]⁺; 342 [²⁰⁵TiL]⁺; 340 [²⁰³TiL]⁺; 298 [²⁰⁵TiL – CO₂]⁺; 296 [²⁰³TiL – CO₂]⁺; 205 [²⁰⁵Ti]⁺; 203 [²⁰³Ti]⁺; 137 [HL]⁺; 119, [HL – H₂O]⁺.

Thallium(I) 2-amino-3/4-methyl-benzoate, 2 and 3. The preparation follows the procedure given for compound **1** with 3/4-methyl-anthranilic acid (0.483 g, 3.2 mmol each) and Tl₂CO₃ (0.75 g, 1.6 mmol each); yield 0.99/0.56 g (87/49%). Calcd. for C₈H₈NO₂Tl, **2**: C 27.10, H 2.27, N 3.95, Tl 57.65, O 9.03; found: C 27.05, H 2.29, N 3.94, Tl 57.10, O 9.62% (from the difference to 100%). Calcd. for C₈H₉NO_{2.5}Tl, **3**: C 26.43, H 2.50, N 3.85, Tl 56.21, O 11.00; found: C 26.66, H 2.36, N 3.87, Tl 56.40, O 10.71% (from the difference to 100%). IR (KBr, cm⁻¹) for **2**: 3500–2900, m, ν (C–H), ν (N–H); 1603, s, ν_{asym} (C–O), ν (C=C); 1528, m, ν (C=C); 1462, s, ν (C=C); 1423, m, ν (C=C); 1375, s, ν_{sym} (C–O); 1314, s, δ (O–H); 1240, m, δ (=C–H); 1082, m, δ (=C–H); 998, m, δ (=C–H); 890, m, γ (=C–H); 834, m, γ (=C–H); 750, m, γ (=C–H); 630, m, ν (CO₂). IR (KBr, cm⁻¹) for **3**: 3435, s, ν (O–H); 3320, s, ν_{asym} (N–H); 3009, m, ν_{sym} (N–H); 1622, s, ν_{asym} (C–O), δ (N–H); 1583, s, ν (C=C); 1508, s, ν (C=C); 1425, s, ν (C=C); 1368, s, ν_{sym} (C–O); 1325, s, ν (C–N); 1254, m, δ (C–H); 1177, m, δ (C–H); 1149, s, δ (C–H); 950, m, γ (C–H); 856, s, γ (C–H); 778, s, γ (C–H); 698, m, γ (C–H); 664, m, γ (C–H); 607, m, ν (CO₂). MS (CI) for compounds **2** and **3**; L = deprotonated ligand; (*) observable in the spectrum of compound **2** only: *m/z* = 915 [3 ²⁰⁵TiL – 3 CO₂ – NH₃ + H]⁺; 913 [2 ²⁰⁵TiL + ²⁰³TiL – 3 CO₂ – NH₃ + H]⁺; 560 [²⁰⁵TiL + ²⁰⁵Ti]⁺; 558 [²⁰⁵TiL + ²⁰³Ti]⁺; 556 [²⁰³TiL + ²⁰³Ti]⁺; 471(*) [²⁰⁵TiL + HL – NH₃ – H₂O]⁺; 469(*) [²⁰³TiL + HL – NH₃ – H₂O]⁺; 355 [²⁰⁵TiL]⁺; 353 [²⁰³TiL]⁺; 311 [²⁰⁵TiL – CO₂]⁺; 309(*) [²⁰³TiL – CO₂]⁺; 267(*) [2 HL – NH₃ – H₂O]⁺; 205 [²⁰⁵Ti]⁺; 203 [²⁰³Ti]⁺; 151 [HL]⁺; 133 [HL – H₂O]⁺; 107 [HL – CO₂]⁺.

Thallium(I) 2-hydroxy-benzoate, 4. Preparation, elemental analysis and IR (KBr): ref 4. MS (CI); L = deprotonated ligand: *m/z* = 668 (2 ²⁰⁵TiL – H₂O + H)⁺; 666 (²⁰⁵TiL + ²⁰³TiL – H₂O + H)⁺; 548 (²⁰⁵TiL + ²⁰⁵Ti)⁺; 546 (²⁰⁵TiL + ²⁰³Ti)⁺; 544 (²⁰³TiL + ²⁰³Ti)⁺; 464

(²⁰⁵TiL + HL – H₂O + H)⁺; 343 (²⁰⁵TiL)⁺; 341 (²⁰³TiL)⁺; 326 (²⁰⁵TiL – H₂O + H)⁺; 324 (²⁰³TiL – H₂O + H)⁺; 205 (²⁰⁵Ti)⁺; 203 (²⁰³Ti)⁺; 138 (HL)⁺; 121 (HL – H₂O + H)⁺.

Thallium(I) 2-Hydroxy-3/4-methyl-benzoate, 5 and 6. As described for **1**, using 3/4-methyl-salicylic acid (0.487 g, 3.2 mmol each) and Tl₂CO₃ (0.75 g, 1.6 mmol each) in 30 mL of water; yield 0.94/1.06 g (82/93%). Calcd. for C₈H₇O₃Tl: C 27.03, H 1.98, Tl 57.49, O 13.50; found: C 26.90/27.01, H 1.97/1.99, Tl 56.95/57.49, O 14.18/13.51% (from the difference to 100%). IR (KBr, cm⁻¹) for compound **5**: 3500–2900, m, ν (C–H), ν (O–H); 1606, s, ν_{asym} (C–O), ν (C=C); 1557, m, ν (C=C); 1478, s, ν (C=C); 1441, m, ν (C=C); 1405, s, ν_{sym} (C–O); 1296, s, δ (O–H); 1255, m, δ (C–H); 1078, m, δ (C–H); 999, m, δ (C–H); 912, m, γ (C–H); 834, m, γ (C–H); 779, m, γ (C–H); 745, s, γ (C–H); 639, m, γ (O–H); 573, m, ν (CO₂). IR (KBr, cm⁻¹) for compound **6**: 3500–2500, m, ν (C–H), ν (O–H); 1644, s, ν_{asym} (C–O), ν (C=C); 1596, m, ν (C=C); 1504, s, ν (C=C); 1437, m, ν (C=C); 1375, s, ν_{sym} (C–O); 1300, s, δ (O–H); 1255, m, δ (C–H); 1171, m, δ (C–H); 1091, m, δ (C–H); 947, m, γ (C–H); 886, m, γ (C–H); 778, m, γ (C–H); 704, s, γ (C–H); 618, m, γ (O–H); 592, m, ν (CO₂). MS (CI) for compounds **5** and **6**; L = deprotonated ligand: *m/z* = 765 [2 ²⁰⁵TiL + ²⁰⁵Ti – 2 CO₂ – 2 H₂O – 2 CH₂]⁺; 763 [2 ²⁰⁵TiL + ²⁰³Ti – 2 CO₂ – 2 H₂O – 2 CH₂]⁺; 561 [²⁰⁵TiL + ²⁰⁵Ti]⁺; 559 [²⁰⁵TiL + ²⁰³Ti]⁺; 557 [²⁰³TiL + ²⁰³Ti]⁺; 356 [²⁰⁵TiL]⁺; 354 [²⁰³TiL]⁺; 339 [²⁰⁵TiL – H₂O + H]⁺; 337 [²⁰³TiL – H₂O + H]⁺; 313 [²⁰⁵TiL – CO₂ + H]⁺; 311 [²⁰³TiL – CO₂ + H]⁺; 205 [²⁰⁵Ti]⁺; 203 [²⁰³Ti]⁺; 152 [HL]⁺; 135 [HL – H₂O + H]⁺; 108 [HL – CO₂]⁺.

X-ray Structure Determination. The crystalline samples were placed in an inert oil, mounted on a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated with an Enraf-Nonius DIP 2020 image plate system (Silicon-Graphics O2 workstation) with monochromated Mo K α (λ = 0.71073 Å) radiation at –130 °C. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares calculations on *F*² with SHELXL-97. Non-H-atoms were refined with anisotropic

thermal parameters. Protons of the water molecule in thallium(I) 2-amino-4-methyl-benzoate were neglected; all other H-Atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Extinction corrections were applied for all the presented compounds using DELABS. A summary of the crystal data, experimental details and refinement results is listed in Table 1. Important interatomic distances and angles are given in the corresponding figure captions. Thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDS-202884 to CCDS-202888, respectively.

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Supporting Information Available: X-ray crystallographic files for **1**, **2**, **3**, **5**, and **6** (CIF). Crystal data, data collection, structure refinement, thermal parameters, and complete tables of interatomic distances and angles for **1**, **2**, **3**, **5**, and **6** (PDF, 26 pages, print/PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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