Abstract: Two new benzene tricarboxylato derivatives \([\text{[Cy}_2\text{NH}_2]\text{[C}_6\text{H}_3\text{(CO}_2\text{)}_3]\cdot4\text{H}_2\text{O} \ (1)\) and \([\text{[i-Bu}_2\text{NH}_2]\text{[Me}_3\text{SnO}_2\text{C}]_2\text{C}_6\text{H}_3\text{CO}_2] \ (2)\) have been synthesized and characterized by X-ray crystallography. In the solid state, compound 1 shows a three-dimensional structure involving intra- and intermolecular hydrogen bonds, whereas the X-ray structure of 2 consists of pentacoordinated Sn centers bonded to three methyl groups and two O atoms in a trans-O\text{Sn}C\text{e} environment, bridged by oxyanions leading to a layered structure; the cation is involved in intramolecular hydrogen bonds.

Keywords: hydrogen bonds; organotin; 3D and layered structures; tricarboxylate.

Introduction

The multifunctional ligand derived by deprotonation of benzene-1,3,5-tricarboxylic acid has been widely used for the manufacture of microporous materials (Yaghi et al., 1996; Cheng et al., 2004). Thus, some solvated and nonsolvated benzene-1,3,5-tricarboxylato metal derivatives have been reported, for example, \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{bis(methanol)-tris(trimethyltinIV)}])\) and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(methanol-trimethyltinIV)}])\) (Ma et al., 2005), \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{bis(dimethylsulfoxide-trimethyltinIV)}])\) dimethylsulfoxide solvate (Dakternieks et al., 2002), \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triethylenetinIV)}])\) and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triphenyltinIV)}])\) ethanol solvate dihydrate (Ma et al., 2005), and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triphenyltinIV)}])\) dichloromethane diethylether solvate (Ma et al., 2005) and catena \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{bis(trimethyltinIV))]}\) monohydrate (Ma et al., 2005).

The chemistry of organotin (IV) derivatives is still the subject of many studies linked to various applications in the areas of medicine, industry, and agriculture (Ayrey and Poller, 1980; Owen, 1980; Blunden et al., 1984; Gielen, 1985; Crowe, 1994; Gielen et al., 1995). With this aim, several supramolecular organotin compounds have been synthesized and characterized (Chandrasekhar et al., 2003; Kapoor et al., 2005; Herntrich and Merzweiler, 2006). In our laboratory, some of them containing SnMe3 and SnPh3 residues have been recently published (Diop et al., 2011, 2012; Sow et al., 2012a,b). In this context, we have recently published a supramolecular trimethyltinIV tricarboxylate \([\text{[Cy}_2\text{NH}_2]\text{[1-Me}_3\text{(H}_2\text{O)}\text{SnOCO}_3\text{C}_6\text{H}_3\text{(OOC)}\text{2}]\text{EtOH}} \ (Ndoye et al., 2012). Thus, in a continuation of these works, we have initiated here the study of the interactions between both 1,3,5-(HOOC)3C6H3 and Cy2NH and between \([\text{[i-Bu}_2\text{NH}_2]\text{[1,3,5-(OOC)}\text{3C}_6\text{H}_3\text{(OOC)}\text{2}]\text{Cl}\text{Me}_3\text{Sn}_2])\) and \([\text{[i-Bu}_2\text{NH}_2]\text{[1,3,5-(OOC)}\text{3C}_6\text{H}_3\text{(OOC)}\text{2}]\text{Cl}\text{Me}_3\text{Sn}_2])\), which have yielded the title derivatives for which X-ray structures have been determined.

Results and discussion

The structure of 1 consists of a three-dimensional (3D) network involving intra- and intermolecular hydrogen bonds (Figure 1). Every tricarboxylato anion is surrounded for the manufacture of microporous materials (Yaghi et al., 1996; Cheng et al., 2004). Thus, some solvated and nonsolvated benzene-1,3,5-tricarboxylato metal derivatives have been reported, for example, \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{bis(methanol)-tris(trimethyltinIV))]}\) and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(methanol-trimethyltinIV))]}\) (Ma et al., 2005), \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(dimethylsulfoxide-trimethyltinIV))]}\) dimethylsulfoxide solvate (Dakternieks et al., 2002), \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triethylenetinIV))]}\) and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triphenyltinIV))]}\) ethanol solvate dihydrate (Ma et al., 2005), and \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{tris(triphenyltinIV))]}\) dichloromethane diethylether solvate (Ma et al., 2005) and catena \([\mu\text{-benzene-1,3,5-tricarboxylato}-\text{bis(trimethyltinIV))]}\) monohydrate (Ma et al., 2005).
in a diverse network of hydrogen bonds, with only the water molecule (containing O7) not forming the maximum of three such interactions. Thus, the water molecule (containing O7) only hydrogen bonds to one other water molecule (containing O8) and one carboxylic acid moiety (containing C9), and not at all as H-bond receptor. The O8 atom links to two water molecules and one carboxylic acid moiety, while

Table 1 Hydrogen-bond geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tr>
<td>O7—H7A···O8i</td>
<td>0.98 (2)</td>
<td>1.89 (2)</td>
<td>2.845 (2)</td>
<td>166 (3)</td>
</tr>
<tr>
<td>O7—H7B···O5</td>
<td>0.89 (2)</td>
<td>1.87 (2)</td>
<td>2.7582 (19)</td>
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<tr>
<td>O8—H8A···O3</td>
<td>0.91 (2)</td>
<td>2.07 (2)</td>
<td>2.9586 (19)</td>
<td>165 (3)</td>
</tr>
<tr>
<td>O8—H8B···O9</td>
<td>0.89 (2)</td>
<td>1.89 (2)</td>
<td>2.7692 (19)</td>
<td>172 (2)</td>
</tr>
<tr>
<td>O9—H9B···O2</td>
<td>0.85 (2)</td>
<td>1.96 (2)</td>
<td>2.8062 (18)</td>
<td>174 (2)</td>
</tr>
<tr>
<td>O9—H9A···O4ii</td>
<td>0.87 (2)</td>
<td>1.92 (2)</td>
<td>2.7590 (17)</td>
<td>163 (2)</td>
</tr>
<tr>
<td>O10—H10A···O6</td>
<td>0.87 (2)</td>
<td>1.81 (2)</td>
<td>2.6773 (18)</td>
<td>171 (2)</td>
</tr>
<tr>
<td>O10—H10B···O3iii</td>
<td>0.89 (2)</td>
<td>2.06 (2)</td>
<td>2.9259 (17)</td>
<td>167 (2)</td>
</tr>
<tr>
<td>N1—H1A···O4ii</td>
<td>0.93 (2)</td>
<td>1.96 (2)</td>
<td>2.8746 (18)</td>
<td>168.5 (17)</td>
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<tr>
<td>N1—H1B···O2</td>
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<td>1.84 (2)</td>
<td>2.7743 (17)</td>
<td>163.0 (17)</td>
</tr>
<tr>
<td>N2—H2A···O10</td>
<td>1.00 (2)</td>
<td>1.78 (2)</td>
<td>2.7756 (19)</td>
<td>173.5 (16)</td>
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<td>N2—H2B···O1</td>
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<td>1.81 (2)</td>
<td>2.7038 (17)</td>
<td>167.4 (18)</td>
</tr>
<tr>
<td>N3—H3A···O6</td>
<td>0.91 (2)</td>
<td>1.82 (2)</td>
<td>2.7182 (18)</td>
<td>170.5 (17)</td>
</tr>
<tr>
<td>N3—H3B···O3iii</td>
<td>0.900 (19)</td>
<td>1.99 (2)</td>
<td>2.8869 (18)</td>
<td>172.7 (16)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) -x+1, y+1/2, z+3/2; (ii) -x+1, y-1/2, z+3/2; (iii) -x+3/2, y+2, z+1/2.

Figure 3 The asymmetric unit of compound 2; only the major component of the disordered cation is shown for clarity.

Selected bond distances (Å): Sn(1)-O(1): 2.2322(15); Sn(1)-O(5′): 2.2975(15), Sn(2)-O(3) 2.1670(16), Sn(2)-O(2″) 2.4046(16), O(1)-C(7): 1.273(3); O(2)-C(7): 1.242(3); O(3)-C(9): 1.280(3): O(4)-C(9): 1.242(3); O(5)-C(8): 1.266(3); O(6)-C(8): 1.249(3); angles (°): C(11)-Sn(1)-C(12) 125.20(14), C(11)-Sn(1)-C(10) 115.75(18), C(12)-Sn(1)-C(10) 118.87(19), C(11)-Sn(1)-O(1) 96.64(9), C(12)-Sn(1)-O(1) 90.70(9), C(10)-Sn(1)- O(1) 86.52(10), C(11)-Sn(1)-O(5′) 91.25(8), C(12)-Sn(1)-O(5′) 88.58(9), C(10)-Sn(1)-O(5′) 85.82(10), O(1)-Sn(1)-O(5′) 170.82(6), C(11)-Sn(2)-C(13) 117.14(15), C(14)-Sn(2)-C(13) 116.75(15), C(15)-Sn(2)-C(13) 125.09(12), C(14)-Sn(2)-O(3) 87.13(9), C(15)-Sn(2)-O(3) 97.65(9), C(13)-Sn(2)-O(3) 94.68(9), C(14)-Sn(2)-O(2″) 85.13(9), C(15)-Sn(2)-O(2″) 88.56(9), O(3)-Sn(2)-O(2″) 172.26(6). Symmetry operations: (′) x-1, y, z; (″) -x+1/2, y-1/2, z; (′″) x+1/2, y, z.
the water molecule (containing O9) H-bonds to two carboxylic acids (containing C7 and C8) and one water molecule (containing O8). The water molecule (containing O10) links with two carboxylic acid groups (containing C8 and C9) and one cation (containing N2). The overall network is a reticular grid (Figure 2); the relevant geometric data relating to these hydrogen bonds are given in Table 1.

In 2, each of the two tin atoms is five-coordinated by two carboxylate oxygen atoms derived from the triscarboxylate ligand, which are in apical positions, and to three methyl groups occupying the equatorial positions of a trigonal bipyramid (Figure 3). There are two types of carboxylate groups in the structure: one which is bidentate involving C7 and two monodentate carboxylates based on C8 and C9. There are two types of tin centers with a trigonal bipyramidal environment in the molecule, although they have similar geometries but different O-Sn-O angles – O1-Sn1-O5′ [170.82°(6)] and O2-Sn2-O2″ [172.26°(6)] angles show that the O-Sn-O frameworks deviate from linearity. The almost planar SnMe3 skeletons [ΣC-Sn-C angles: 359.82, 358.98°] are bridged by the carboxylate O atoms, leading to a layered structure. Thus, the layered structure is composed of tetranuclear rings in which the noncoordinated carboxylate O atoms (O4 and O6) are involved in hydrogen bonds with NH groups of i-Bu₂NH⁺ cations, which lie within these macrocycles [H1A...O6, 1.784 Å; H1B...O4, 1.862 Å], offset from their centers to allow bonding to the two carboxylate groups at one corner (Figure 4). The Sn-O bond lengths between the bridging ligand and the tin centers [2.322(15), 2.2975(15), 2.4046(16), and 2.1670(16) Å, respectively, for Sn1-O1, Sn1-O5′, Sn2-O2, and Sn2-O3″] are in the range of reported Sn-O distances (Diassé-Sarr et al., 2004; Alvarez Boo et al., 2006). The structure of [(Me₃SnO₂C)₂C₆H₃CO₂] [i-Bu₂NH⁺] (2) can be compared with the related species (Me₃SnO₂C)₂C₆H₃CO₂H·H₂O (Ma et al., 2005). Although the framework formed by the [1,3-(Me₃SnO₂C)₂-6-(OOC)C₆H₃]- anion is similar in both cases, the remaining counterions [i-Bu₂NH⁺]¹ or [H₃O⁺]¹ impart quite different lattice structures. Thus, while [i-Bu₂NH⁺]¹ hydrogen bonds to two carboxylate groups within the same plane, generating layers independent of each other, the [H₃O⁺]¹ species forms hydrogen bonds between layers, generating a 3D structure.

Figure 4 Lattice structure of compound 2.
The isobutyl groups on nitrogen have been omitted for clarity.
Crystal data and structure refinement

Details of the crystallographic data are given in Table 2. In both cases, data were collected at 150(2) K using Mo-kα radiation (λ=0.71073 Å). Refinement was full-matrix least-squares based on F2; the absorption correction was semiempirical from equivalents. In the final cycles of least-squares refinement, all nonhydrogen atoms were allowed to vibrate anisotropically. Specific details for the two structures are as follows: 1: Water molecule hydrogen atoms have been located in the difference Fourier map and were refined freely with idealized bond lengths. 2: Hydrogen atoms when included at calculated positions were relevant, save for those of the NH2 group, which were located in the difference map and refined. Disorder in the cation in the ratio 65:35 required the C21A-C21A bond length to be constrained. The structure has been solved by SHELXS and refined by SHELXL (Sheldrick et al., 1986, 1997).

Experimental

All chemicals were purchased from Aldrich (Germany) and used without any further purification. The following abbreviations are used: vs (very strong), s (strong), m (medium), sh (shoulder), br (broad).

Synthesis of [(Cy2-NH)3.C6H3(CO2)3·4H2O]

[(i-C6H4)2NH2.C6H3(CO2)3·4H2O] was obtained on neutralizing an aqueous solution of benzene-1,3,5-tricarboxylic acid with i-C6H4NH2 in a 1:3 ratio; after a water evaporation at 60°C, crystals (m.p. = 205°C) were collected (yield, 92%). Elemental analysis: found (calc. for C23H41NO6Sn2): C: 65.60 (65.42), H: 9.97 (10.13), N: 5.04 (5.09). Infrared data (cm⁻¹): 3442 s (br) (v(OH)); 2936 vs v(NH2); 1637 vs, 1600 vs (COO) as; 1355 vs v(COO).s.

Synthesis of [Bu2-NH]2[C6H3(CO2)2CO2H·0.5H2O]

[i-Bu2NH]2[C6H3(CO2)3·0.5H2O] was obtained on neutralizing benzene-1,3,5-tricarboxylic acid with i-ButNH2 in water in a 1:3 ratio; a white powder is collected after solvent evaporation at 60°C. When an aqueous solution of [i-Bu2NH]2[C6H3(CO2)3·0.5H2O] was mixed with an ethanolic solution of SnMe3Cl in 1:2 molar ratio, a clear solution was obtained, which was stirred for 2 h. When this solution was submitted to a slow solvent evaporation, crystals of [i-Bu2NH]2[C6H3(CO2)3.SnMe3]2 suitable for X-ray study were obtained (yield, 72%); m.p. 220°C. Elemental analysis: found (calc. for C45H83N3O10.Sn2): C: 60.95 (61.54), H: 6.74 (6.21), N: 2.86 (2.11). Infrared data (cm⁻¹): 3541 s (br) (v(OH)); 2962 vs v(NH2); 1618 vs, 1568 s (COO) as; 1351 vs, 1402 sh v(COO).s.

References


