X-ray crystal structures of 

\[ [(\text{Cy}_2\text{NH}_2)]_3[\text{C}_6\text{H}_3(\text{CO}_2)]_3 \cdot 4\text{H}_2\text{O} \] 
and 

\[ [\text{i-Bu}_2\text{NH}_2][\text{(Me}_3\text{SnO}_2\text{C})_2\text{C}_6\text{H}_3\text{CO}_2] \]

**Abstract:** Two new benzene tricarboxylato derivatives \([\text{Cy}_2\text{NH}_2]][\text{C}_6\text{H}_3(\text{CO}_2)]_3 \cdot 4\text{H}_2\text{O} (1)\) 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 \(\text{trans-O}_2\text{SnC}_3\) environment, bridged by oxoanions leading to a layered structure; the cation is involved in intramolecular hydrogen bonds.

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

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**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, \([\mu_1\text{-benzene-1,3,5-tricarboxylato-bis(methanol)-tris(trimethylinvin)](IV)}\) and \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(methanoltrimethylinvin)](IV)}\) (Ma et al., 2005), \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(dimethylsulfoxide-trimethylinvin)](IV)}\) dimethylsulfoxide solvate (Dakternieks et al., 2002), \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(tribenzylinvin)](IV)}\) and \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(triphenylvin)](IV)}\) ethanol solvate dihydrate (Ma et al., 2005), and \([\mu_1\text{-benzene-1,3,5-tricarboxylato-tris(triphenylvin)](IV)}\) dichloromethane diethylether solvate (Ma et al., 2005) and catena \([\mu_3\text{-benzene-1,3,5-tricarboxylato-bis(trimethylinvin)](IV)}\) 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 trimethylvin(IV) tricarboxylate \([\text{Cy}_2\text{NH}_2][\text{1-Me}(\text{H}_2\text{O})\text{SnOCO-3,5-(OOC)}_2\text{C}_6\text{H}_3]\cdot \text{EtOH}\) (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 \([\text{i-Bu}_2\text{NH}_2][\text{1,3,5-}\text{(OOC)}_3\text{C}_6\text{H}_3]\) and SnMe₃Cl, 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, \([\mu_1\text{-benzene-1,3,5-tricarboxylato-bis(methanol)-tris(trimethylinvin)](IV)}\) and \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(methanoltrimethylinvin)](IV)}\) (Ma et al., 2005), \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(dimethylsulfoxide-trimethylinvin)](IV)}\) dimethylsulfoxide solvate (Dakternieks et al., 2002), \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(tribenzylinvin)](IV)}\) and \([\mu_3\text{-benzene-1,3,5-tricarboxylato-tris(triphenylvin)](IV)}\) ethanol solvate dihydrate (Ma et al., 2005), and \([\mu_1\text{-benzene-1,3,5-tricarboxylato-tris(triphenylvin)](IV)}\) dichloromethane diethylether solvate (Ma et al., 2005) and catena \([\mu_3\text{-benzene-1,3,5-tricarboxylato-bis(trimethylinvin)](IV)}\) monohydrate (Ma et al., 2005).

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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></th>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D—A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<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>
<td></td>
</tr>
<tr>
<td>O7—H7B···O5</td>
<td>0.89 (2)</td>
<td>1.87 (2)</td>
<td>2.7582 (19)</td>
<td>175 (4)</td>
<td></td>
</tr>
<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>
<td></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>
<td></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>
<td></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>
<td></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>
<td></td>
</tr>
<tr>
<td>O10—H10B···O3ii</td>
<td>0.89 (2)</td>
<td>2.06 (2)</td>
<td>2.9259 (17)</td>
<td>167 (2)</td>
<td></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 (3)</td>
<td></td>
</tr>
<tr>
<td>N1—H1B···O2</td>
<td>0.96 (2)</td>
<td>1.84 (2)</td>
<td>2.7743 (17)</td>
<td>163.0 (17)</td>
<td></td>
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<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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</tr>
<tr>
<td>N2—H2B···O1</td>
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<td>1.81 (2)</td>
<td>2.7038 (17)</td>
<td>167.4 (18)</td>
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<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>
<td></td>
</tr>
<tr>
<td>N3—H3B···O3ii</td>
<td>0.900 (19)</td>
<td>1.99 (2)</td>
<td>2.8869 (18)</td>
<td>172.7 (16)</td>
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</tr>
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</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.
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 O₁-Sn₁-O₂ [172.26°(6)] angles show that the O-Sn-O frameworks deviate from linearity. The almost planar SnMe₃ skeletons [ΣC-Sn₁-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 tetrannuclear rings in which the noncoordinated carboxylate O atoms (O₄ and O₆) are involved in hydrogen bonds with NH₂ 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 [2.2322(15), 2.2975(15), 2.4046(16), and 2.1670(16) Å, respectively, for Sn₁-O₁, Sn₁-O₅, Sn₁-O₆, and Sn₁-O₂] 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⁺] or [H₃O⁺] impart quite different lattice structures. Thus, while [i-Bu₂NH⁺] hydrogen bonds to two carboxylate groups within the same plane, generating layers independent of each other, the [H₃O⁺] species forms hydrogen bonds between layers, generating a 3D structure.
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 [(Cy₂NH₂)₃C₆H₃(CO₂)₃·4H₂O]

[(Cy₂NH₂)₃C₆H₃(CO₂)₃·4H₂O] was obtained on neutralizing an aqueous solution of benzene-1,3,5-tricarboxylic acid with Cy₂NH 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 C₆H₃(CO₂)₃Sn) 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 ν(CO₂)s; 1351 vs ν(CO₂)s.

Synthesis of [Bu₂NH₂][C₆H₃(CO₂)₃(SnMe₃)₂]·(DMSO)

[iBu₂NH₂][C₆H₃(CO₂)₃(SnMe₃)₂]·(DMSO) was obtained on neutralizing an aqueous solution of benzene-1,3,5-tricarboxylic acid with i-Bu₂NH in water in a 1:3 ratio; a white powder is collected after solvent evaporation at 60°C. When an aqueous solution of [i-Bu₂NH₂][C₆H₃(CO₂)₃(SnMe₃)₂]·(DMSO) 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-Bu₂NH₂][C₆H₃(CO₂)₃(SnMe₃)₂] suitable for X-ray study were obtained (yield, 72%); m.p. 220°C. Elemental analysis: found (calc. for C₂₃H₄₁NO₆Sn₂): C: 60.95 (61.54), H: 6.74 (6.21), N: 2.44 (2.11)%. Infrared data (cm⁻¹): 3442 s (br) v(OH); 2962 vs v(NH₂); 1618 vs, 1600 vs ν(CO₂)s; 1351 vs ν(CO₂)s.

References


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