Supramolecular organotin tris-carboxylates: crystal and molecular structure of \([\text{Cy}_2\text{NH}_2]_2[\text{1-Me}_3(\text{H}_2\text{O})\text{SnOCO-3,5-(OOC)}_2\text{C}_6\text{H}_3] \cdot \text{EtOH}\)

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Abstract
The crystal and molecular structure of \([\text{Cy}_2\text{NH}_2]_2[\text{C}_6\text{H}_3(\text{CO}_2)_3\text{SnMe}_3\cdot \text{H}_2\text{O}]\cdot \text{CH}_3\text{CH}_2\text{OH} \,(1)\) has been determined by single crystal X-ray diffraction analysis. In this compound, the tin atom is pentacoordinated by three methyl groups, one oxygen atom of a water molecule and one oxygen atom deriving from the tris-carboxylato ligand, in a \(\text{trans}\)-coordinated \(\text{O}_2\text{SnC}_3\) environment. The dicyclohexylammonium cations \([\text{O}(3), \text{O}(6)]\) are involved in stronger hydrogen bonds with the non-coordinated oxygen atoms of the carboxylate, while, along with hydrogen bonds involving water and ethanol, gives rise to a complex 3D lattice structure.

Keywords: carboxylate; organotin; supramolecular; X-ray.

Introduction
Resulting from the various applications of organotin(IV) compounds (Ayre and Poller, 1980; Evans and Karpel, 1985; Alvarez Boo et al., 2006), our groups have been involved in seeking new organo- and halotin(IV) molecules and have reported several papers in this area (Diassé-Sarr et al., 1997, 2004; Diop et al., 2003; Diallo et al., 2009). We have initiated a study of the reactions between salts of a tri-carboxylic acid \([\text{C}_6\text{H}_3(\text{CO}_2)_3\text{Cy}_2\text{NH}_2]_\text{Cl}\) and \(\text{SnMeCl}_2\) to explore the synthesis of new organo- and halotin(IV) molecules and have reported several papers in this area (Diassé-Sarr et al., 1997, 2004; Diop et al., 2003; Diallo et al., 2009). We have initiated a study of the reactions between salts of a tri-carboxylic acid \([\text{C}_6\text{H}_3(\text{CO}_2)_3\text{Cy}_2\text{NH}_2]_\text{Cl}\) and \(\text{SnMeCl}_2\) to explore the supramolecular structures of the resulting compounds. Here, we report the title compound, the structure of which has been determined by single crystal X-ray diffraction analysis.

Results and discussion
The structure (Figure 1) consists of a central benzene-1,3,5-tricarboxylato tri-anion monocoordinating a single \(\text{SnMe}_3\) residue, the metal linked to a water molecule in axial position generating a \(\text{trans}\)-trigonal bipyramidal \(\text{O}_2\text{SnC}_3\) environment; charge balance is achieved through the presence of two \([\text{Cy}_2\text{NH}_2]^+\) cations. The carboxylate bonded to tin is monodentate, reflected in two markedly different C–O bond lengths \([\text{C}(1)−\text{O}(1)\,1.294(2), \text{C}(1)−\text{O}(2)\,1.230(2)\,\text{Å}\] and an \(\text{Sn}(1)−\text{O}(2)\) separation of >3.2 Å. There is less disparity in the C–O bonds of the two remaining carboxylates \([\text{e.g.,}\, \text{C}(8)−\text{O}(5)\,1.267(2), \text{C}(8)−\text{O}(6)\,1.246(2)\,\text{Å}\] both of which are involved in N–H…O hydrogen bonds.

Experimental
\([\text{C}_6\text{H}_3(\text{CO}_2)_3\text{Cy}_2\text{NH}_2]_\text{Cl}\) is obtained on neutralizing benzene-1,2,3-tricarboxylic acid with \(\text{Cy}_2\text{NH}\) in water in 1:3 ratio; a white powder is collected after a solvent evaporation at 60 °C. When an aqueous solution of \([\text{C}_6\text{H}_3(\text{CO}_2)_3\text{Cy}_2\text{NH}_2]_\text{Cl}\) is mixed with ethanolic solution of \(\text{SnMeCl}_2\) in 1:1 ratio, a clear solution is obtained and stirred for no less than 2 h. When submitted to a slow solvent evaporation, this solution yields crystals suitable for an X-ray study. All the chemicals were purchased from Aldrich (Germany) and used without any further purification.

Crystal structure
A crystal of approximate dimensions 0.25×0.25×0.20 mm was used for data collection. Data were collected at 150(2) K using
Figure 1  The structure of compound 1 showing both the asymmetric unit and the formation of a supramolecular lattice based on NH…OC hydrogen bonds.

Mo-Kα radiation (λ=0.71073 Å); full details of the crystallographic experiment are given in Table 1. Refinement was full-matrix least-squares based on F², the absorption correction was semi-empirical from equivalents. In the final cycles of least-squares refinement all non-hydrogen atoms were allowed to vibrate anisotropically. Hydrogen atoms when included at calculated positions were relevant, except for those of the NH₂, EtOH and H₂O groups which were located in the difference map and refined. The structure was solved and refined using the WinGX-1.70 suite of programs (Farrugia, 1999).

Table 1  Crystal data and structure refinement.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula: C₃₈H₆₈N₂O₈Sn</td>
<td></td>
</tr>
<tr>
<td>Formula weight: 799.63</td>
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</tr>
<tr>
<td>Crystal system: Monoclinic</td>
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<tr>
<td>Space group: P 21/n</td>
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</tr>
<tr>
<td>a(Å): 14.19980 (10); b(Å): 20.0718 (2); c(Å): 15.45080 (10); α(°): 90; β(°): 109.7390 (10); γ(°): 90; V(Å³): 4144.96 (6); Z: 4</td>
<td></td>
</tr>
<tr>
<td>ρ(calc (mg/m³): 1.281</td>
<td></td>
</tr>
<tr>
<td>µ(Mo-Kα)(mm⁻¹): 0.665</td>
<td></td>
</tr>
<tr>
<td>F(000): 1696</td>
<td></td>
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<tr>
<td>Reflections collected: 112°643</td>
<td></td>
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<tr>
<td>Independent reflections: 12°017 [R(int) =0.0615]</td>
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<tr>
<td>Reflections observed (&gt;2 σ): 9613</td>
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<td>Absorption correction: Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission: 0.8785, 0.8514</td>
<td></td>
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<tr>
<td>Refinement method: full-matrix least-squares on F²</td>
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<tr>
<td>R-goodness-of-fit on F²: 1.061</td>
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<tr>
<td>Final R indices [I &gt;2 σ(I)]: 0.0324, 0.0694</td>
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<tr>
<td>R indices (all data): 0.0492, 0.0769</td>
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<tr>
<td>Largest diff. peak and hole (e Å⁻³): 0.789 and -0.857</td>
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<tr>
<td>Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); SHELXS97(Sheldrick, 1997); CCDC deposition number: 826325</td>
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</tr>
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</table>

Figure 2  The lattice structure of 1 showing intermolecular hydrogen bonds (dotted lines). Hydrogen bond data.
References


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