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Supramolecular organotin tris-carboxylates: crystal and molecular structure of $[\text{C}_6\text{H}_5\text{NH}_2]_2[\text{1-Me}_3(\text{H}_2\text{O})\text{SnOCO-3,5-(OOC)}_2\text{C}_6\text{H}_3]\cdot\text{EtOH}$

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Abstract

The crystal and molecular structure of $[\text{C}_6\text{H}_5\text{NH}_2]_2[\text{C}_6\text{H}_3(\text{CO}_2)_3\text{SnMe}_3\cdot\text{H}_2\text{O}]\cdot\text{CH}_3\text{CH}_2\text{OH}$ (**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 *trans*-coordinated O_2SnC_3 environment. The dicyclohexylammonium cations are involved in intermolecular 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 (Ayrey 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 $[\text{C}_6\text{H}_3(\text{CO}_2)_3\cdot(\text{C}_6\text{H}_5\text{NH}_2)_3]$ and SnMe_3Cl 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 SnMe_3 residue, the metal linked to a water molecule in axial position

generating a *trans*-trigonal bipyramidal O_2SnC_3 environment; charge balance is achieved through the presence of two $[\text{C}_6\text{H}_5\text{NH}_2]^+$ cations. The carboxylate bonded to tin is monodentate, reflected in two markedly different C–O bond lengths [C(1)–O(1) 1.294(2), C(1)–O(2) 1.230(2) Å] and an Sn(1)–O(2) separation of >3.2 Å. There is less disparity in the C–O bonds of the two remaining carboxylates [e.g., C(8)–O(5) 1.267(2); C(8)–O(6) 1.246(2) Å], both of which are involved in N–H...O hydrogen bonds.

Selected bond lengths [Å] and angle (°): Sn–C(10) 2.116(2); Sn–C(11) 2.120(2); Sn–C(12) 2.1276(19), Sn–O(1) 2.1631(12); Sn–O(7) 2.3747(13) Å; C(10)–Sn–C(11) 123.27(11); C(10)–Sn–C(12) 119.32(9); C(11)–Sn–C(12) 116.34(10); C(10)–Sn–O(1) 94.71(7); C(11)–Sn–O(1) 96.63(8); C(12)–Sn–O(1) 88.72(6); C(10)–Sn–O(7) 85.76(7); C(11)–Sn–O(7) 88.02(8); C(12)–Sn–O(7) 85.90(6); O(1)–Sn–O(7) 174.06(5)°. Symmetry operations: 'x-1/2, -y-1/2, 1/2+z; '' 1-x, -y, 2-z; ''' 1/2-x, -y-1/2, z-1/2.

The lattice structure of **1** (Figure 2) involves a complex pattern of hydrogen bonds. Each cation is linked to a carbonyl oxygen through each of its hydrogen atoms, e.g., N(1)–H(1A) and N(1)–H(1B), both link to O(5) at relatively short distances [N(1)...O(5): 2.814(2), 2.778(2) Å], along with a weaker hydrogen bond from one of the centers, e.g., N(1)–H(1A)...O(6), N(1)...O(6): 3.323(2) Å; an analogous pattern is repeated at N(2). The water molecule hydrogen bonds through H(7A) to another carbonyl oxygen [O(3)] and the ethanol [O(8)], while the latter hydrogen bonds through H(8) to the remaining carbonyl group, O(6). Thus, the carbonyl groups most weakly hydrogen bonded to the ammonium cations [O(3), O(6)] are involved in stronger hydrogen bonds to either water or ethanol.

Experimental

$[\text{C}_6\text{H}_3(\text{CO}_2)_3\cdot(\text{C}_6\text{H}_5\text{NH}_2)_3]$ is obtained on neutralizing benzene-1,2,3-tricarboxylic acid with $\text{C}_6\text{H}_5\text{NH}_2$ in water in 1:3 ratio; a white powder is collected after a solvent evaporation at 60°C. When an aqueous solution of $[\text{C}_6\text{H}_3(\text{CO}_2)_3\cdot(\text{C}_6\text{H}_5\text{NH}_2)_3]$ is mixed with ethanolic solution of SnMe_3Cl 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

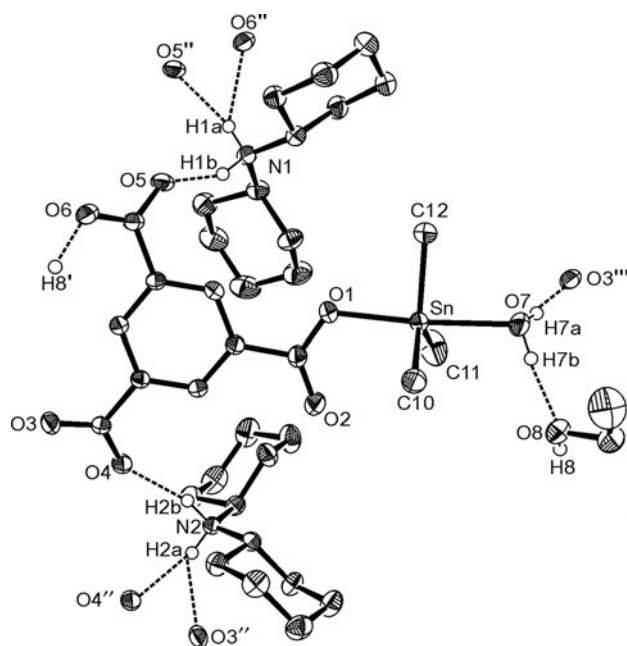


Figure 1 The structure of compound **1** showing both the asymmetric unit and the formation of a supramolecular lattice based on NH...OC hydrogen bonds.

Mo- k_{α} radiation ($\lambda=0.71073$ Å); full details of the crystallographic experiment are given in Table 1. Refinement was full-matrix least-squares based on F^2 , the absorption correction was semi-empirical from equivalents. In the final cycles of least-

Table 1 Crystal data and structure refinement.

Empirical formula:	$C_{38}H_{68}N_2O_8Sn$
Formula weight:	799.63
Crystal system:	Monoclinic
Space group:	P 21/n
a(Å):	14.19980 (10); b(Å): 20.0718 (2); c(Å): 15.45080 (10);
$\alpha(^{\circ})$:	90; $\beta(^{\circ})$: 109.7390 (10); $\gamma(^{\circ})$: 90; V(Å ³): 4144.96 (6) ^o ;
Z:	4 ρ_{calc} (mg/m ³): 1.281
$\mu(\text{Mo-}k_{\alpha})(\text{mm}^{-1})$:	0.665 ^o
F(000):	1696
Reflections collected:	112 ^o 643
Independent reflections:	12 ^o 017 [R(int)=0.0615]
Reflections observed (>2 sigma):	9613
Absorption correction:	Semi-empirical from equivalents
Max. and min. transmission:	0.8785, 0.8514
Refinement method:	full-matrix least-squares on F^2
Goodness-of-fit on F^2 :	1.061
Final R indices [I > 2 sigma(I)]:	0.0324, 0.0694
R indices (all data):	0.0492, 0.0769
Largest diff. peak and hole (e Å ⁻³):	0.789 and -0.857
Program(s) used to solve structure:	SHELXS97 (Sheldrick, 1990); SHELXS97(Sheldrick, 1997);
CCDC deposition number:	826325

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 NH_2 , EtOH and H_2O 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).

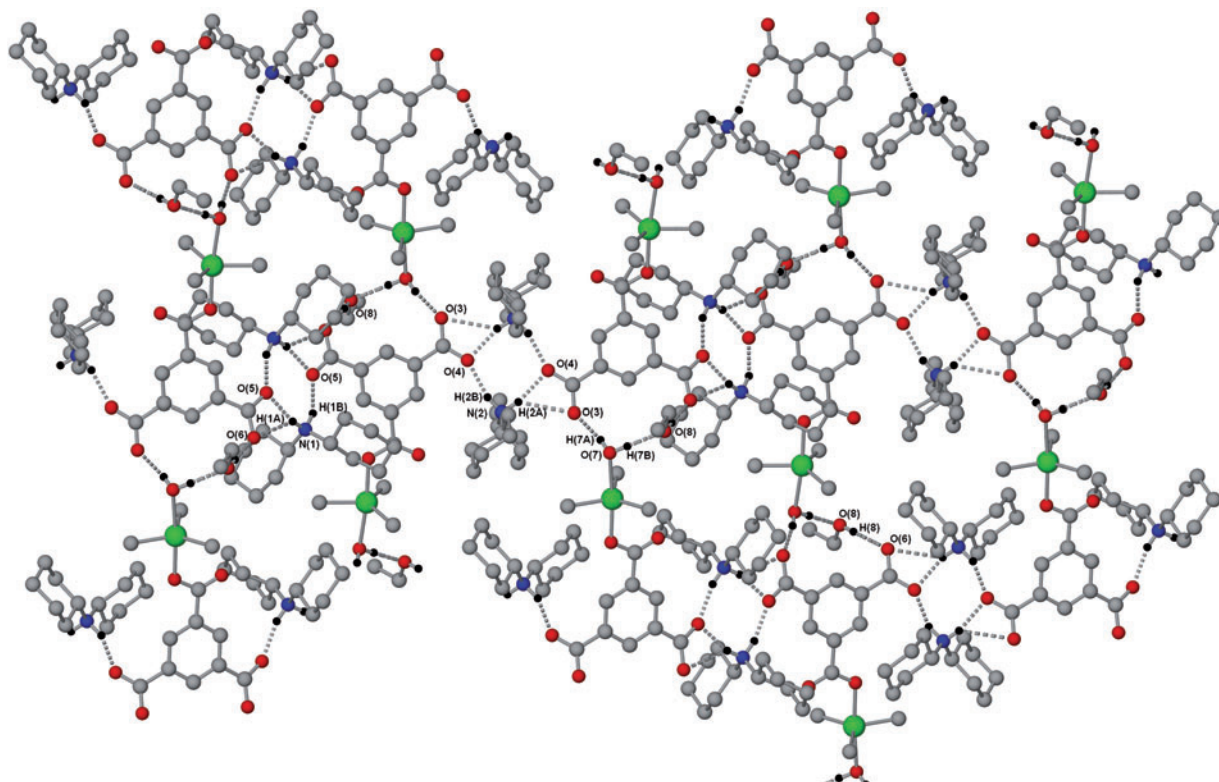


Figure 2 The lattice structure of **1** showing intermolecular hydrogen bonds (dotted lines). Hydrogen bond data.

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