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X-ray crystal structures of $[(Cy_2NH_2)]_3[C_6H_3(CO_2)_3]\cdot 4H_2O$ and $[i\text{-}Bu_2NH_2][(Me_3SnO_2C)_2C_6H_3CO_2]$

Abstract: Two new benzene tricarboxylato derivatives $[(Cy_2NH_2)]_3[C_6H_3(CO_2)_3]\cdot 4H_2O$ (**1**) and $[i\text{-}Bu_2NH_2][(Me_3SnO_2C)_2C_6H_3CO_2]$ (**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_2SnC_3 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.

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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, [(μ$_4$-benzene-1,3,5-tricarboxylato)-bis(methanol)-tris(trimethyltin(IV))] and [(μ$_3$-benzene-1,3,5-tricarboxylato)-tris(methanol-trimethyltin(IV))] (Ma et al., 2005), [(μ$_3$-benzene-1,3,5-tricarboxylato)-tris(dimethylsulfoxide-trimethyltin(IV))] dimethylsulfoxide solvate (Dakternieks et al., 2002), [(μ$_3$-benzene-1,3,5-tricarboxylato)-tris(tribenzyltin(IV))] and [(μ$_3$-benzene-1,3,5-tricarboxylato)-tris(triphenyltin(IV))] ethanol solvate dihydrate (Ma et al., 2005), [(μ$_3$-benzene-1,3,5-tricarboxylato)-tris(triphenyltin(IV))] dichloromethane diethylether solvate (Ma et al., 2005) and catena [(μ$_3$-benzene-1,3,5-tricarboxylato)-bis(trimethyltin(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 $SnMe_3$ and $SnPh_3$ residues have been recently published (Diop et al., 2011, 2012; Sow et al., 2012a,b). In this context, we have recently published a supramolecular trimethyltin(IV) triscarboxylate $[Cy_2NH_2]_2[1\text{-}Me_3(H_2O)SnOCO\text{-}3,5\text{-}(OOC)_2C_6H_3]\cdot EtOH$ (Ndoye et al., 2012). Thus, in a continuation of these works, we have initiated here the study of the interactions between both $1,3,5\text{-}(HOOC)_3C_6H_3$ and Cy_2NH and between $[i\text{-}Bu_2NH_2]_3[1,3,5\text{-}(OOC)_3C_6H_3]$ and $SnMe_3Cl$, 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 tricarboxylate anion is surrounded by three dicyclohexyl ammonium cations involving N_1, N_2 and N_3. The N_1- and N_3-containing cations are involved in eight-membered ring formation, whereas that based on the N_2-containing cation forms a 12-membered ring. A fourth 12-membered ring involving two water molecules (containing O_8 and O_9) and two carboxylic acid groups (containing C_7 and C_8) and a fifth 14-membered ring involving three water molecules (containing O_7, O_8 and O_9) and two carboxylic acids (containing C_8 and C_9) complete the hydrogen bond network. Two cations (containing N_1 and N_2) are hydrogen-bonded to a carboxylic acid and a water molecule while the cation (containing N_3) hydrogen bonds to two carboxylic acid groups. The water molecules are also involved

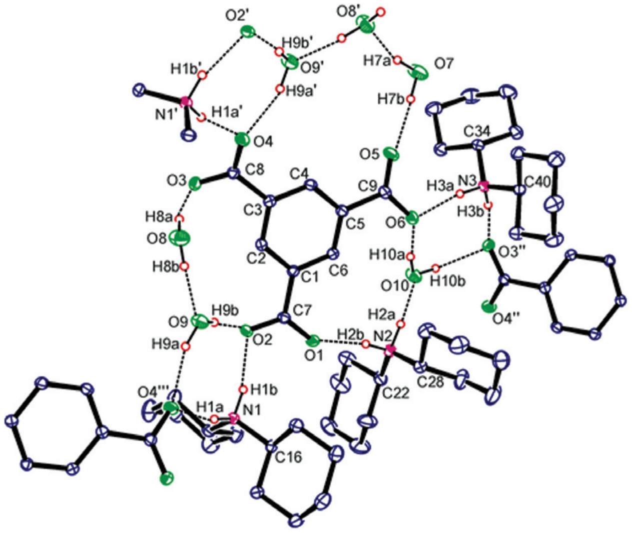

Figure 1 The asymmetric unit of compound **1.**
Selected bond distances (Å): O(1)-C(7): 1.2482(18); O(2)-C(7): 1.2635(18); O(3)-C(8): 1.2647(18); O(4)-C(8): 1.2543(19); O(5)-C(9): 1.2307(19); O(6)-C(9): 1.273(2); angles (°): O(1)-C(7)-O(2): 123.98(14); O(4)-C(8)-O(3): 123.73(14); O(5)-C(9)-O(6): 124.54(14). Symmetry operations: (′) 1-*x*, 1/2+*y*, 3/2-*z*; (″) 3/2-*x*, 2-*y*, 1/2+*z*; (‴) -*x*, *y*-1/2, 3/2-*z*.

in a diverse network of hydrogen bonds, with only the water molecule (containing O_7) not forming the maximum of three such interactions. Thus, the water molecule (containing O_7) only hydrogen bonds to one other water molecule (containing O_8) and one carboxylic acid moiety (containing C_9), and not at all as H-bond receptor. The O_8 atom links to two water molecules and one carboxylic acid moiety, while

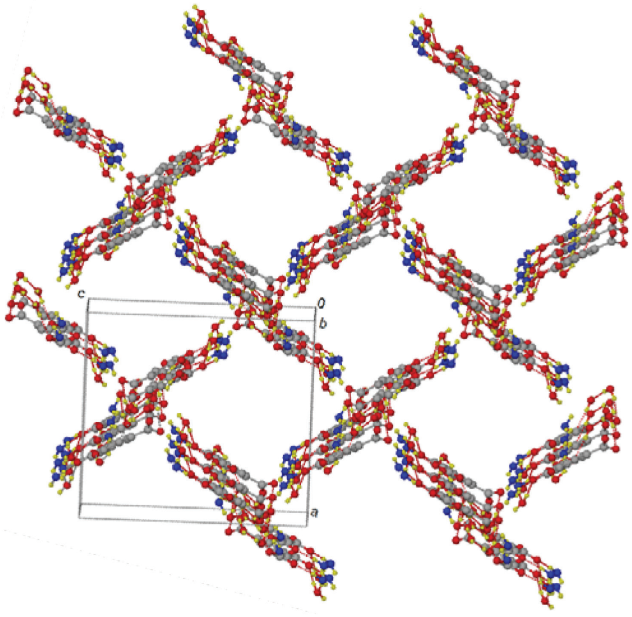

Figure 2 3D structure of compound **1**.

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

D—H···A	*D*—H	H···A	*D*···A	*D*—H···A
O7—H7A···O8^{i}	0.98 (2)	1.89 (2)	2.845 (2)	166 (3)
O7—H7B···O5	0.89 (2)	1.87 (2)	2.7582 (19)	175 (4)
O8—H8A···O3	0.91 (2)	2.07 (2)	2.9586 (19)	165 (3)
O8—H8B···O9	0.89 (2)	1.89 (2)	2.7692 (19)	172 (2)
O9—H9B···O2	0.85 (2)	1.96 (2)	2.8062 (18)	174 (2)
O9—H9A···O4^{ii}	0.87 (2)	1.92 (2)	2.7590 (17)	163 (2)
O10—H10A···O6	0.87 (2)	1.81 (2)	2.6773 (18)	171 (2)
O10—H10B···O3^{iii}	0.89 (2)	2.06 (2)	2.9259 (17)	167 (2)
N1—H1A···O4^{ii}	0.93 (2)	1.96 (2)	2.8746 (18)	168.5 (17)
N1—H1B···O2	0.96 (2)	1.84 (2)	2.7743 (17)	163.0 (17)
N2—H2A···O10	1.00 (2)	1.78 (2)	2.7756 (19)	173.5 (16)
N2—H2B···O1	0.91 (2)	1.81 (2)	2.7038 (17)	167.4 (18)
N3—H3A···O6	0.91 (2)	1.82 (2)	2.7182 (18)	170.5 (17)
N3—H3B···O3^{iii}	0.900 (19)	1.99 (2)	2.8869 (18)	172.7 (16)

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.

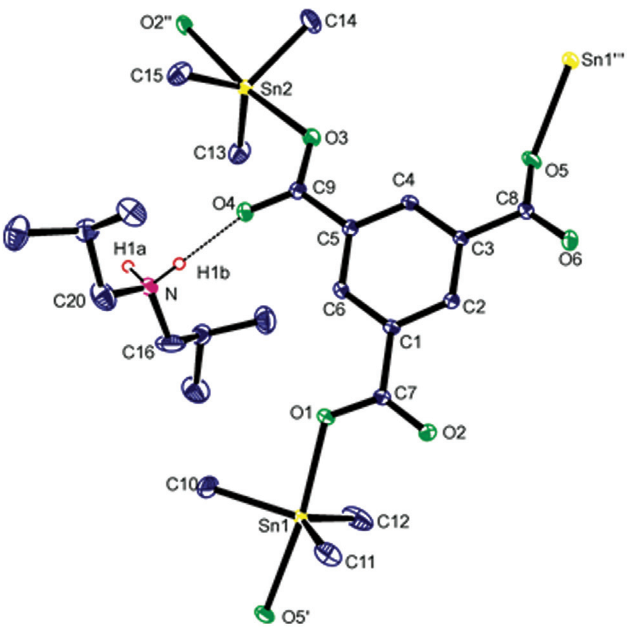

Figure 3 The asymmetric unit of compound **2**; only the major component of the disordered cation is shown for clarity.
Selected bond distances (Å): Sn(1)-O(1): 2.2322(15); Sn(1)-O(5′): 2.2975(15), Sn(2)-O(3) 2.1670(16), Sn(2)-O(2″) 2.4046(16), O(1)-C(7): 1.273(3); O(2)-C(7): 1.242(3); O(3)-C(9): 1.280(3): 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(14)-Sn(2)-C(15) 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″) 86.16(9), C(13)-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, (‴) 1+*x*, *y*, *z*.

the water molecule (containing O_9) H-bonds to two carboxylic acids (containing C_7 and C_8) and one water molecule (containing O_8). The water molecule (containing O_{10}) links with two carboxylic acid groups (containing C_8 and C_9) and one cation (containing N_2). 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 C_7 and two monodentate carboxylates based on C_8 and C_9. 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 – O_1-Sn_1-$O_{5'}$ [170.82°(6)] and O_3-Sn_2-$O_{2''}$ [172.26°(6)] angles show that the O-Sn-O frameworks deviate from linearity. The almost planar $SnMe_3$ skeletons [ΣC-Sn_1-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 (O_4 and O_6) are involved in hydrogen bonds with NH_2 groups of *i*-$Bu_2NH_2^+$ cations, which lie within these macrocycles [H_{1A}...O_6, 1.784 Å; H_{1B}...O_4, 1.862 Å], offset from their centers to allow bonding to the two carboylate 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 Sn_1-O_1, Sn_1-$O_{5'}$, Sn_2-O_2, and Sn_2-$O_{3''}$] are in the range of reported Sn-O distances (Diassé-Sarr et al., 2004; Alvarez Boo et al., 2006). The structure of $[(Me_3SnO_2C)_2C_6H_3CO_2]$ [*i*-Bu_2NH_2] (**2**) can be compared with the related species $(Me_3SnO_2C)_2C_6H_3CO_2H{\cdot}H_2O$ (Ma et al., 2005). Although the framework formed by the $[1,3\text{-}(Me_3SnO_2C)_2\text{-}6\text{-}(OOC)C_6H_3]^-$ anion is similar in both cases, the remaining countercations [*i*-$Bu_2NH_2]^+$ or $[H_3O]^+$ impart quite different lattice structures. Thus, while [*i*-$Bu_2NH_2]^+$ hydrogen bonds to two carboxylate groups within the same plane, generating layers independent of each other, the $[H_3O]^+$ species forms hydrogen bonds between layers, generating a 3D structure.

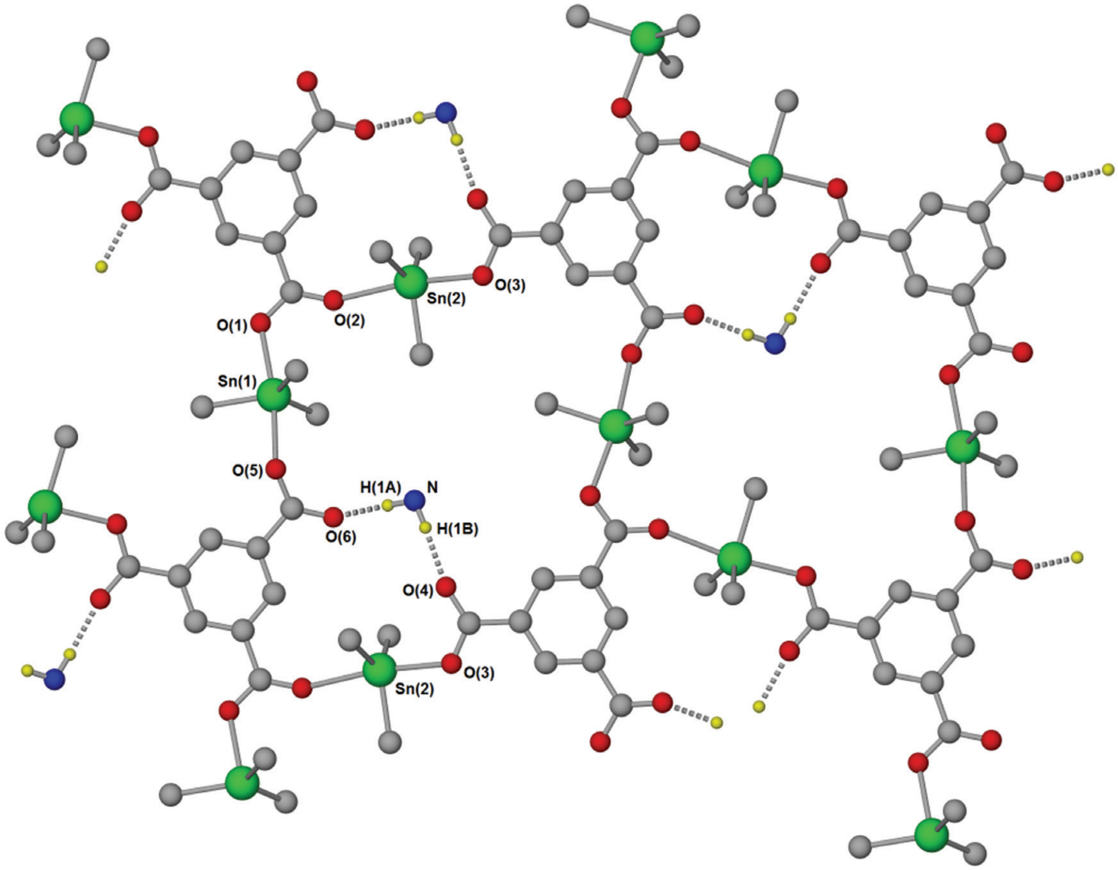

Figure 4 Lattice structure of compound **2**.
The isobutyl groups on nitrogen have been omitted for clarity.

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-k_α radiation (λ=0.71073 Å). Refinement was full-matrix least-squares based on F^2; 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 NH_2 group, which were located in the difference map and refined. Disorder in the cation in the ratio 65:35 required the C_{21A}-C_{23A} bond length to be constrained. The structure has been solved by SHELXS and refined by SHELXL (Sheldrick et al., 1986, 1997).

Table 2 Crystallographic data for compounds **1** and **2**.

	1	2
Empirical formula	$C_{45}H_{83}N_3O_{10}$	$C_{23}H_{41}NO_6Sn_2$
Formula mass	826.14	664.95
Crystal system	Orthorhombic	Monoclinic
a (Å)	16.0886(3)	11.3431(1)
b (Å)	16.5114(3)	20.0231(2)
c (Å)	17.8039(3)	13.0078(2)
β (°)		101.845(1)
Unit cell volume (Å^3)	4729.52(15)	2891.47(6)
Space group	$P2_12_12_1$	$P2_1/n$
No. of formula units per unit cell, *Z*	4	4
Absorption coefficient, μ (mm^{-1})	0.081	1.760
No. of reflections measured	66,180	59,114
No. of independent reflections	10,782	8411
R_{int}	0.0749	0.0429
Final R_1 values [$I>2\sigma(I)$]	0.0401	0.0307
Final $wR(F^2)$ values [$I>2\sigma(I)$]	0.0832	0.0651
Final R_1 values (all data)	0.0608	0.0434
Final $wR(F^2)$ values (all data)	0.0928	0.0700
Goodness of fit on F^2	1.030	1.080
CCDC number	826324	924039

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 $[(Cy_2NH_2)_3C_6H_3(CO_2)_3\cdot 4H_2O]$

$[(Cy_2NH_2)_3C_6H_3(CO_2)_3\cdot 4H_2O]$ was obtained on neutralizing an aqueous solution of benzene-1,3,5-tricarboxylic acid with Cy_2NH 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 $C_{45}H_{83}N_3O_{10}$): C: 65.60 (65.42), H: 9.97 (10.13), N: 5.04 (5.09)%. Infrared data (cm^{-1}): 3442 s (br) ν(OH); 2936 vs ν(NH_2); 1637 vs, 1600 vs ν(COO)as; 1355 vs ν(COO)s.

Synthesis of $[^i\text{Bu}_2NH_2]^+[C_6H_3(CO_2)_3(SnMe_3)_2]^-$

$[i\text{-}Bu_2NH_2]_2[C_6H_3(CO_2)_2CO_2H]\cdot 0.5H_2O$ was obtained on neutralizing benzene-1,3,5-tricarboxylic acid with *i*-Bu_2NH in water in a 1:3 ratio; a white powder is collected after solvent evaporation at 60°C. When an aqueous solution of $[i\text{-}Bu_2NH_2]_2[C_6H_3(CO_2)_2CO_2H]\cdot 0.5H_2O$ was mixed with an ethanolic solution of $SnMe_3Cl$ 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 $[i\text{-}Bu_2NH_2][C_6H_3(CO_2)_3(SnMe_3)_2]$ (**2**) suitable for X-ray study were obtained (yield, 72%; m.p. 220°C). Elemental analysis: found (calc. for $C_{23}H_{41}NO_6Sn_2$): C: 40.95 (41.54), H: 6.74 (6.21), N: 2.44 (2.11)%. Infrared data (cm^{-1}): 3541 m (br) ν(OH); 2962 vs ν(NH_2); 1618 vs, 1568 s ν(COO)as; 1351 vs, 1402 sh ν(COO)s.

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