Main Group Met. Chem., 2012;34(5-6):127–130 © 2012 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/mgmc-2011-0018

Crystal and molecular structure of diorganoammonium oxalatotrimethylstannate, $[R_2NH_2][Me_3Sn(C_2O_4)]$ (R=*i*-Bu, cyclohexyl)

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Abstract

The title compounds $[R_2NH_2][C_2O_4SnMe_3]$(R=*i*-Bu, Cy), in which tin atoms adopt a distorted trigonal bipyramidal configuration, have been prepared and submitted to an X-ray diffraction study. These compounds have been obtained from the reaction of $(Cy_2NH_2)_2C_2O_4{\cdot}H_2O$ or $(i\text{-}Bu_2NH_2)_2C_2O_4$ with $SnMe_3Cl$. In both $[R_2NH_2][C_2O_4SnMe_3]$ compounds, the trans complex has an almost regular trigonal bipyramidal geometry around the tin atom. The $SnMe_3$ residues are connected as a chain with bridging oxalate anions in a *trans*-SnC_3O_2 framework, the oxygen atoms being in axial positions. The cations connect linear adjacent chains through NH…O hydrogen bonds giving layered structures.

Keywords: bridging oxalate; hydrogen bonds; layered structures; X-ray structure.

Introduction

Applications of organotin (IV) compounds are very well known (Evans and Karpel, 1985; Kapoor et al., 2005; Zhang et al., 2006). The mononuclear derivatives of the general formula $[R_4N][AO_4SnPh_3]$(A=S, Se, Cr, W) have been synthesized and studied spectroscopically by our group (Gueye et al., 1993; Sall et al., 1995; Diop et al., 2000, 2002; De Barros et al., 2009, 2010; Diallo et al., 2009a,b; Qamar-Kane et al., 2009; Fall et al., 2010), but dealing with their $SnMe_3$ residue containing homologue, to the best of our knowledge, only $[Et_4N][WO_4SnMe_3]$ has been reported (De Barros et al., 2009). We have also published the X-ray structure of $(SnMe_3)_2C_2O_4{\cdot}2H_2O$ (Sidibé et al., 1998) and have initiated here the study of the interactions between $[R_2NH_2]_2C_2O_4{\cdot}nH_2O$ (*n*=1, 2) (R=*i*-Bu, Cy) with $SnMe_3Cl$, which has yielded crystals suitable for X-ray structure determination. Ng and Rae (2000) and Ng and Hook (1999) have reported the crystal structure of $[Cy_2NH_2][C_2O_4SnPh_3]$.

Results and discussion

As a continuation of our attempts to obtain new oxalato-SnR_3 (R=Me, Bu, Ph) residue-containing compounds, we report here the study of the interactions of $(R_2NH_2)_2C_2O_4{\cdot}nH_2O$ (*n*=1, 2) (R=*i*-Bu, Cy) and $SnMe_3Cl$, which have yielded two derivates of formulae $[R_2NH_2][C_2O_4SnMe_3]$. In both compounds of $[R_2NH_2][C_2O_4SnMe_3]$ [R=*i*-Bu (**1**), Cy (**2**)], the crystallographic study reveals a polymeric structure with bridging oxalate ligands, the *trans*-C_3SnO_2 framework with oxygen in axial positions being in an almost perfect trigonal bipyramidal environment. In a recent paper, we have published the spectroscopic work on $[i\text{-}Bu_2NH_2][C_2O_4SnPh_3]$. In $[i\text{-}Bu_2NH_2][C_2O_4SnMe_3]$, the anion $[C_2O_4SnMe_3]^-$ is present as an infinite chain with bridging oxalates and planar $SnMe_3$ residues. The neighboring chains are then connected by cations through N-H…O hydrogen bonds (one between two chains), leading to a layered structure.

In $[Cy_2NH_2][C_2O_4SnMe_3]$ (**2**), the anion $[C_2O_4SnMe_3]^-$ is also present as an infinite chain like in compound **1**. Therefore, in this compound, the infinite chains are connected two by two by the cations in such way that the two cations are linked to the same oxygen atoms, whereas in $Cy_2NH_2C_2O_4SnPh_3$, the cations are linked to different oxygen atoms.

In $[i\text{-}Bu_2NH_2][C_2O_4SnMe_3]$ (**1**), the bond distances [Sn-O 2.2815(18), 2.2828(19) Å] are identical and different [Sn-O(1) 2.215(2), 2.295(2) and Sn-O(2) 2.238(2), 2.315(2) Å] in $[Cy_2NH_2][C_2O_4SnMe_3]$. The O-Sn-O angle in (**1**) is close to the ideal angle of a trans trigonal bipyramid [178.88(8)°], whereas the one in (**2**) [172.90(7)°] deviates sensitively. Both the equatorial planes are defined by the three methyl groups [Sn-C 2.113(3), 2.120(3), 2.123(3) Å and 2.113(3), 2.120(3), 2.123(3) Å in **1** and **2**, respectively]. The sum of the equatorial angles also in both is close to 360° [359.99° (**1**), 359.4° (**2**)], indicating a perfectly planar $SnMe_3$ group. In **1**, the $[C_2O_4SnMe_3]^-$ anion chains are connected by the cations through NH…O hydrogen bond, leading to a layered structure. In these compounds, the C-O bond distances of the oxygen atom involved in hydrogen bond or directly linked to the tin atom [1.235–1.271 Å (**1**), 1.25–1.27 Å (**2**)] are longer than the C=O bond distances involving free oxygen of the oxalate. Thus, each oxalate has two oxygen atoms directly linked to $SnMe_3$ residues and two involved in hydrogen bonds. The C-O bond distances in the both [C-O(1) 1.271,

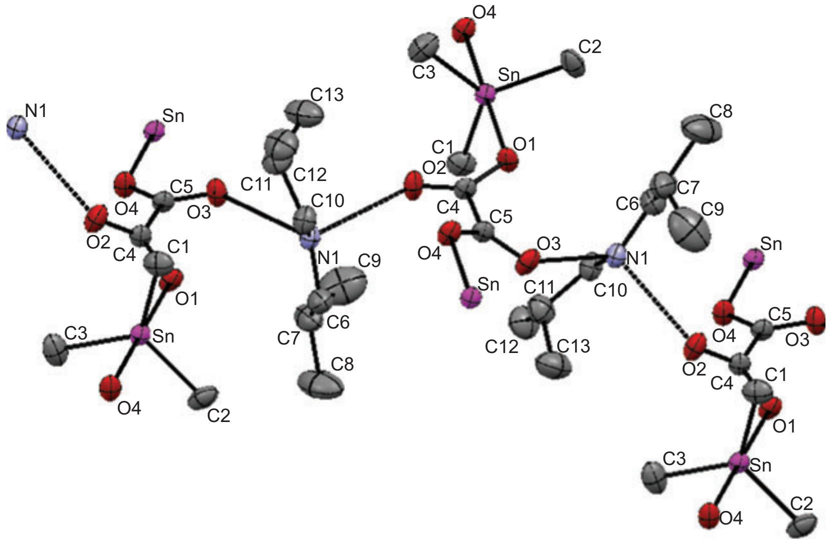

Figure 1 Two-dimensional structure of $[i\text{-Bu}_2\text{NH}_2\text{C}_2\text{O}_4\text{SnMe}_3]_\infty$. Selected bond distances: Sn-C(1)2.113(3); Sn-C(2)2.120(3); Sn-C(3)2.123(3); Sn-O(1) 2.2815(18); Sn-O(4)#12.2828(19); O(1)-C(4) 1.271(3) O(2)-C(4)1.237(4) O(3)-C(5) 1.235(4); O(4)-C(5)1.269(3); O(4)-Sn#2 2.2827(19); N(1)-C(6)1.485(4). Selected bond angles: C(1)-Sn-C(2)123.84(15); C(1)-Sn-C(3)122.79(16); C(2)-Sn-C(3)113.36(17); C(1)-Sn-O(1)90.11(10) C(2)-Sn-O(1)86.47(10); C(3)-SnO(1)94.25(10); C(1)-Sn-O(4)#1 88.93(10); C(2)-Sn-O(4)#1 93.58(10); C(3)-Sn-O(4)#1 86.76(10); O(1)-Sn-O(4)#1 178.88(8); C(4)-O(1)-S 117.83(17); C(5)-O(4)-Sn#2 118.02(18). Symmetry transformations used to generate equivalent atoms: #1 *x*+1, *y*, *z* #2 *x*-1, *y*, *z*.

C-O(2) 1.237, C-O(3) 1.235 and C-O(4) 1.269 Å (**1**) and C-O(3) 1.262, C-O(1) 1.278, C-O(2) 1.221 and C-O(4) 1.25 Å (**2**)] reflect well the free double C=O_2, the double bond involved in hydrogen bonds, and the C-O single bonds with the charged oxygen atoms (Figures 1 and 2). The two structures are mainly different in the involvement of the cations. In **1**, all the oxygen atoms not involved in σ bonding participate in hydrogen bonding, whereas in **2**, a pair of cations connects alternatively two chains, leaving a free oxygen atom in each oxalate involved in neither the σ bonding nor H-bonding.

Conclusion

In the two studied compounds, the $[\text{SnMe}_3\text{C}_2\text{O}_4]_\infty^-$ complex anions are connected as infinite chain. The fundamental difference in these two structure is the way the cation is involved for building the hydrogen bonds network (their $[\text{SnPh}_3\text{C}_2\text{O}_4]^-$ known homologue contains oxalate monochelating SnPh_3 residue).

Experimental section

Synthesis

$(\text{R}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot n\text{H}_2\text{O}$ have been prepared by completely neutralizing oxalic acid with i-Bu_2NH or Cy_2NH in water and collecting the white powder after a slow water evaporation. When the neutral $(\text{R}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot n\text{H}_2\text{O}$ (R=i-Bu, Cy) had been mixed with SnMe_3Cl (Aldrich) in absolute ethanol, colorless solutions were obtained. When submitted to a slow solvent evaporation, colorless crystals suitable for X-ray structure determination were obtained. All the

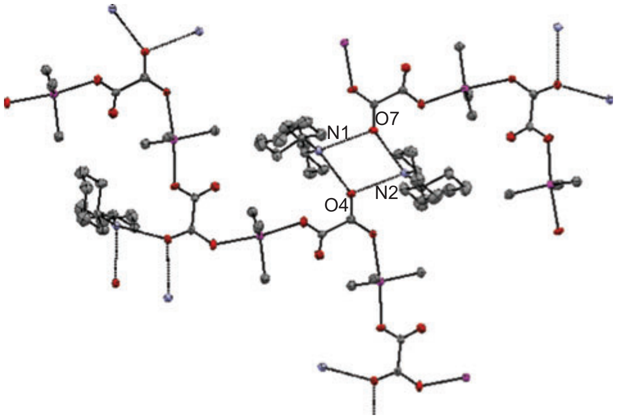

Figure 2 The lattice structure of **2** showing the pattern of hydrogen bonds. Geometric data: Selected bond distances: Sn(1)-C(2)2.112(3); Sn(1)-C(3)2.128(3); Sn(1)-C(1)2.130(3); Sn(1)O(1)2.215(2); Sn(1)O(8)#12.295(2); Sn(2)-C(7)2.109(3); Sn(2)C(6)2.127(3); Sn(2)C(8)2.135(3); Sn(2)-O(5)2.238(2)Sn(2)-O(3)2.315. Selected bond angles: C(2)-Sn(1)-C(3) 116.63(13); C(2)-Sn(1)-C(1)133.50(13); C(3)-Sn(1)-C(1)109.27(13); C(2)-Sn(1)-O(1)92.43(11); C(3)-Sn(1)-O(1)99.88(11); C(1)-Sn(1)-O(1)86.67(10); C(2)-Sn(1)-O(8)#1 86.48 (11); C(3)-Sn(1)-O(8)# 186.86(11); C(1)-Sn(1)-O(8)#189.00(10); O(1)-Sn(1)-O(8)#1172.90(8); C(7)-Sn(2)-C(6)132.45(13); C(7)-Sn(2)-C(8)114.49(13); C(6)-Sn(2)-C(8)112.35(13); C(7)-Sn(2)-O(5) 92.08(11); C(6)-Sn(2)-O(5)86.78(10); C(8)-Sn(2)-O(5)100.93(10); C(7)-Sn(2)-O(3)87.59(10); C(6)-Sn(2)-O(3)88.20(10); C(8)-Sn(2)-O(3)85.63(10);O(5)-Sn(2)-O(3)172.90(7);C(4)-O(1)-Sn(1)118.6(2); C(5)-O(3)-Sn(2)131.88(19); C(9)-O(5)-Sn(2)118.31(19); C(10)-O(8)-Sn(1)#2 134.83(19)Hydrogen bonds N1-H1D 2.842; N1-H1E 2.777; N2-H2D 2.763; N2-H2D 3.409; N2-H2E 2.787. Symmetry transformations used to generate equivalent atoms:#1 *x*+1, *y*, *z* #2 x-1, *y*, *z*.

Table 1 Crystal data and structure refinement.

Empirical formula $C_{13}H_{29}NO_4Sn$; formula weight 382.06; Crystal system monoclinic; Crystal size 0.15×0.15×0.10 mm; Space group P $2_1/c$; a (Å) 7.5775 (2); b (Å) 14.0308 (3) β=97.87°; C (Å) 17.6638 (5); V 1860.36 (8) $Å^3$; Z=4; Diffractometer Nonius KappaCCD; (2); μ 1.382 mm^{-1}; Dcalc 1.364 $g\cdot cm^{-3}$; F (000) 784; Ind Reflns, R_{int} 20567, 0.0342; θ_{max} 27.45°; Obs. Reflns 4212; R (F), RW (F) 0.0377, 0.0806; FinalRindices [I>2 sigma (I)] 0.0335, 0.0772°; Refinement method Full-matrix least-squares on F^2; ρ, $eÅ^{-3}$ 1.407 and -0.761; Trans. factors 0.8742, 0.8195; SHELXS-86; SHELXL-97 (5a, b); Deposition number: 840654

Table 2 Crystal data and structure refinement.

Empirical formula $C_{34}H_{66}N_2O_8Sn_2$; Formula weight 868.27; Crystal system Monoclinic; Crystal size 0.60×0.30×0.10 mm; Space group P $2_1/n$; a (Å) 12.1122 (2); b (Å) 19.9480 (4) β=107.901°; c (Å) 17.7241 (3); V 4075.08 (13) $Å^3$; Z=4; Diffractometer Nonius KappaCCD; μ 1.271 mm^{-1}; F (000) 1792; Dcalc 1.412 $g\cdot cm^{-3}$; Ind Reflns, R_{int} 51078, 0.0715; θ_{max} 27.50°; Obs. Reflns 6073; R (F), RW (F) 0.0667, 0.0812; Final R indices [I>2 sigma(I)] 0.0347, 0.0702; Refinement method Full-matrix least-squares on F^2; ρ, $eÅ^{-3}$ 1.395, -0.997 Trans. factors 0.8834, 0.5159; Programs used SHELXS-86; SHELXL-97 (5a, b); Deposition number: 840653

chemicals were purchased from Aldrich (Germany) and used as such.

Crystal structure determination

Crystals of approximate dimensions 0.15×0.15×0.10 mm (**1**) and 0.60×0.30×0.10 mm (**2**) were used for data collection. Intensity data were collected at 150 K on a Nonius KappaCCD diffractometer (Enraf-Nonius B.V., Rotterdam, The Netherlands) equipped with an Oxford cryostream (Oxford Cryosystems, Oxford, UK), using graphite monochromated Mokα radiation at λ=0.71073 Å. Data were processed using the Nonius Software (Otwinowski and Minor, 1997). A symmetry-related (multi-scan) absorption correction had been applied. Crystal parameters and details on data collection, solution, and refinement for the complexes are provided in Tables 1 and 2. Structure solution followed by full-matrix least-squares refinement was performed using the WinGX-1.80 software suite of programs throughout (Farrugia, 1999). In the final cycles of least-squares refinement, all the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed on calculated positions using a riding model. The structures have been solved by SHELXS-86 and refined by SHELXL-97 (Sheldrick, 1986, 1997). Crystal data are given in Tables 1 and 2. Both H atoms attached to the N of the cation have been located in the difference Fourier map and were freely refined. Schematic views are shown in Figures 1 and 2.

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