

X RAY STRUCTURE OF TETRABUTYLAMMONIUM CHLOROTRIMETHYLTIN HYDROGENOSULPHATE: THE FIRST CYCLIC DIMER HYDROGENOSULPHATO HYDROGEN BONDED ADDUCT

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Abstract: The reaction of trimethyltin (IV) chloride with tetrabutylammonium hydrogenosulphate leads to the formation of $\text{Bu}_4\text{NHSO}_4\cdot\text{SnMe}_3\text{Cl}$, the crystal structure of which has been determined by X-ray analysis. The structure consists of a discrete dimer, in which two hydrogen sulphate anions, each coordinated to a trimethyltin chloride moiety (SnMe_3Cl) are held together by hydrogen bonds. The tin centre displays a *trans* OCIC_3 trigonal bipyramid configuration. Additional infrared, Mössbauer and NMR spectroscopic data are reported.

Keywords: *hydrogenosulphate anion, hydrogen bonded, dimer, infrared, Mössbauer, NMR, X ray diffraction*

INTRODUCTION

The structure of chlorotrimethyltin adducts of O donor [1-5], F donor [6] and N donor [7] ligands, has been reported. The configuration of the tin centre is in all cases trigonal bipyramidal, the methyl groups lying in the equatorial plane. To the best of our knowledge, no oxoanion adduct of SnMe_3Cl has been reported but only related organotin oxy-anions derivatives such as $(\text{SnMe}_3)_2\text{SeO}_3 \cdot \text{H}_2\text{O}$ [8], $(\text{SnMe}_3)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ [9, 10], $(\text{SnMe}_3)_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [11] and $(\text{SnMe}_3)_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ [12]. In KHSO_4 , the anion exists both in dimers and infinite chains forms [13].

In the framework of our research on the coordinating ability of oxoanions, we report here the X-Ray structure determination of $[\text{Bu}_4\text{N}^+]_2[\text{Me}_3\text{Sn}(\text{Cl})(\text{HSO}_4^-)]_2$ together with spectroscopic studies.

EXPERIMENTAL

Materials and spectroscopic methods

$[\text{Bu}_4\text{N}^+][\text{HSO}_4^-]$ and SnMe_3Cl were purchased from Merck and Aldrich Chemicals, respectively, and were both used without further purification.

The elemental analyses (C, H, N) were performed in the Microanalyses Laboratory of the University of Bath (United Kingdom). The experimental details for infrared and Mössbauer spectroscopy and data collecting procedure are reported elsewhere [14, 15]. Infrared data are given in cm^{-1} (abbreviations: (wvs) wide and very strong, (br) broad, (s) strong, (m) medium, (sh) shoulder, (w) weak, (tr) trace). Mössbauer parameters are given in mms^{-1} (abbreviations: I.S = isomer shift, Q.S = quadrupole splitting, Γ = full width at half-height).

Solution NMR spectra were recorded from a saturated CDCl_3 solution, at room temperature, using a Bruker Avance 250 spectrometer, operating at 250.53, 63.00 and 89.27 MHz for ^1H , ^{13}C , and ^{117}Sn , respectively. ^1H , ^{13}C and ^{117}Sn chemical shifts are given in ppm and are referred respectively to SiMe_4 and SnMe_4 , all set to 0.00 ppm. The coupling constants are given in Hz (abbreviations: t = triplet, m = multiplet, dd = doublet of doublets). CP-MAS ^{117}Sn solid-state spectra were recorded at 89.27 MHz on the same spectrometer, with a 4 MAS broad-band probe. Spinning frequencies are chosen between 5 and 9 kHz. A contact time of 1 ms and a recycling delay of 2 s were employed. The chemical shift reference was set with $(\text{cyclo-C}_6\text{H}_{11})_4\text{Sn}$ (-97.35 ppm relative to $(\text{CH}_3)_4\text{Sn}$).

Synthesis of tetrabutylammonium chlorotrimethyltin hydrogenosulphate

$\text{Bu}_4\text{NHSO}_4 \cdot \text{SnMe}_3\text{Cl}$ was obtained on reacting trimethyltin chloride (0.341 mmol in 25 mL ethanol) with tetrabutylammonium hydrogenosulphate (0.341 mmol in 25 mL

ethanol) at room temperature. Crystals suitable for X-ray diffraction of $\text{Bu}_4\text{NH}\text{SO}_4\cdot\text{SnMe}_3\text{Cl}$ were obtained by slow solvent evaporation in methanol solution (ethanol was first evaporated and product then re-dissolved in methanol).

Elemental analyses: [% found (% calc.) for $\text{C}_{19}\text{H}_{46}\text{ClNO}_4\text{SSn}$]: C 42.9 (42.2), H 8.07 (8.65), N 2.68 (2.48).

IR data (cm^{-1}): 2900 wvs (v OH); 1225 s (v S=O); 1161 s (v S=OSn); 1059 s (v S-O); 860 s (v S-OH); 600 w +586 vs (δ SO_3); 436 m (δ S-OH); 549 s (ν_{as} SnC_3); 515 tr (ν_{s} SnC_3).

Mössbauer data (mms^{-1}): I.S = 1.23; Q.S = 2.82; Γ = 1.05

NMR data: ^1H [δ (ppm), $^2\text{J}(^1\text{H}-^{119/117}\text{Sn})$ (Hz)]: Me_3Sn : 0.68, 64/61 (upon dilution: 0.71, 59/61); $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$: 0.95t; 1.40m; 1.60m; 3.23dd; - OSO_3H : 9.34.

^{13}C [δ (ppm, CDCl_3), $^1\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ (Hz)]: Me_3Sn : 1.1, 445/425 (upon dilution: 1.3, 434/414); $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$: 13.6; 19.6; 23.9; 58.6.

^{117}Sn [δ (ppm, CDCl_3)]: 97.2; ^{117}Sn solid state (δ (ppm)): 5.2

X-ray data collection:

Data collection was performed on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-k(radiation ($\lambda = 0.71073 \text{ \AA}$) and a crystal of approximate dimensions 0.30 x 0.45 x 0.45 mm. The structure was solved using direct-methods (SHELXS-86) and was refined by full matrix least-squares method using SHELXTL-97 program [16]. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions, except for that attached to O(4) of the hydrogen sulphate anion, but in later stage of the refinement this also was fixed. One of the two cations in the asymmetric unit shows rotational disorder in the ratio 50:50. In addition, it seems that the crystal undergoes a phase transition at the temperature of the data collection, resulting in all reflections for $l = \text{odd}$ being extremely weak and a relatively poor final R-value. Experimental details on crystal parameters and data collection are given in Table 1; selected bond lengths and angles in Table 2.

RESULTS AND DISCUSSION

Spectroscopic study

The appearance of ν_{s} SnMe_3 as a trace at 515cm^{-1} in the infrared spectrum is indicative of planar SnC_3 groups according to Group Theory [17]. The Mössbauer spectrum consists of a simple doublet of quadrupole splitting 2.82 mms^{-1} and isomer shift of 1.23 mms^{-1} . These data are indicative of a trans pentacoordinated SnC_3 residue [18].

The tin chemical shift in solution (δ ^{117}Sn : 97.2 ppm) is higher than the value in the solid state (5.2 ppm), indicating a higher coordination for tin in the solid state and suggesting that in solution the complex is dissociating into free trimethyltin chloride and tetrabutylammonium hydrogenosulphate. This is confirmed by recording spectra of a diluted sample, in which the ^{117}Sn chemical shift is 131.1 ppm, approaching the value found in literature [19] for $(\text{CH}_3)_3\text{SnCl}$ (164 ppm, $^1\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ 380 Hz, $^2\text{J}(^1\text{H}-^{119/117}\text{Sn})$ 58 Hz). This observation is further corroborated by the change in $^1\text{J}(^{13}\text{C}-^{119/117}\text{Sn})$ and $^2\text{J}(^1\text{H}-^{119/117}\text{Sn})$ coupling constants upon dilution (see experimental part).

Table 1. Crystal and structure refinement data for tetrabutylammonium chlorotrimethyltin hydrogenosulphate

Empirical formula	C ₁₉ H ₄₆ ClNO ₄ SSn
Formula weight	538.77
Crystal system	monoclinic
Space group	C 2/c
<i>a</i> (Å)	25.8160(5)
<i>b</i> (Å)	14.1441(4)
<i>c</i> (Å)	19.3426(5)
β (deg)	128.7030(10)
<i>V</i> (Å ³)	5511.9(2)
<i>V</i> , Calculated density (Mg/m ³)	8, 1.298
μ (Mo-K α) (mm ⁻¹)	1.120
F(000)	2256
Theta range (deg)	5.52 to 27.50
Reflections collected / unique	38443 / 6250 [R(int) = 0.0686]
Final R ₁ , wR ₂ indices [I > 2 σ (I)]	0.059, 0.152
R ₁ , wR ₂ (all data)	0.1212, 0.1985
Largest diff. peak, hole (eÅ ⁻³)	1.208, -0.644

Table 2. Selected bond lengths and angles

Bond lengths [Å]	Sn-C(1)	2.113(8)
	Sn-C(2)	2.091(9)
	Sn-C(3)	2.098(7)
	Sn-O(1)	2.450(5)
	Sn-Cl	2.489(2)
	S-O(1)	1.452(6)
	S-O(2)	1.396(6)
	S-O(3)	1.477(5)
	S-O(4)	1.516(5)
Angles [°]	C(2)-Sn-C(3)	119.7(4)
	C(2)-Sn-C(1)	117.0(4)
	C(3)-Sn-C(1)	122.4(4)
	C(2)-Sn-O(1)	82.8(4)
	C(3)-Sn-O(1)	88.1(3)
	C(1)-Sn-O(1)	89.1(3)
	C(2)- Sn -Cl	91.0(4)
	C(3)- Sn -Cl	93.6(2)
	C(1) -Sn -Cl	95.2(3)
	O(1)- Sn -Cl	173.57(15)
	O(2)-S-O(1)	111.7(4)
	O(2)-S-O(3)	113.9(4)
	O(1)-S-O(3)	109.1(4)
	O(2)-S-O(4)	107.5(4)
	O(1)-S-O(4)	107.5(4)
	O(3)-S-O(4)	106.9(3)
	S-O(1)-Sn	131.5(3)

Crystallographic study

As shown in Figure 1, the structure of tetrabutylammonium chlorotrimethyltin hydrogenosulphate consists of a dimeric anion associated through hydrogen bonds [H(4)---O'(3) = 1.764, O(3)---O(4') 2.533(8) Å; <O(4)-H(4)---O(3') 151.2°] of acetic acid type, interacting electrostatically with two tetrabutylammonium ions. The O---S---O angles are roughly tetrahedral except the O(1)---S---O(3) which is significantly larger [O(1)---S---O(3) = 114.1(5)]. This deviation of about 5° is due to the fact that O(1) is linked to the tin centre [O(1)-Sn = 2.450(5) Å] while O(3) is involved in the hydrogen bond. S---O(2) is the shortest bond [1.396(6) Å] because O(2) is not involved in any other bond and retains its double bond character. The longer S---O(4) bond [1.516(5) Å] when compared to S---O(1) is indicative of the strength of the hydrogen bonds, which also has the effect of reducing the bond order of S-O(3) [1.477(5) Å]. The SnC₃ residue is nearly ideally planar (CSnC angles are in the range 117.0(4) – 122.4(4) °, their sum = 359.2°) as shown by the infrared data, while the OSnCl angle deviates from linearity by *ca.* 7°.

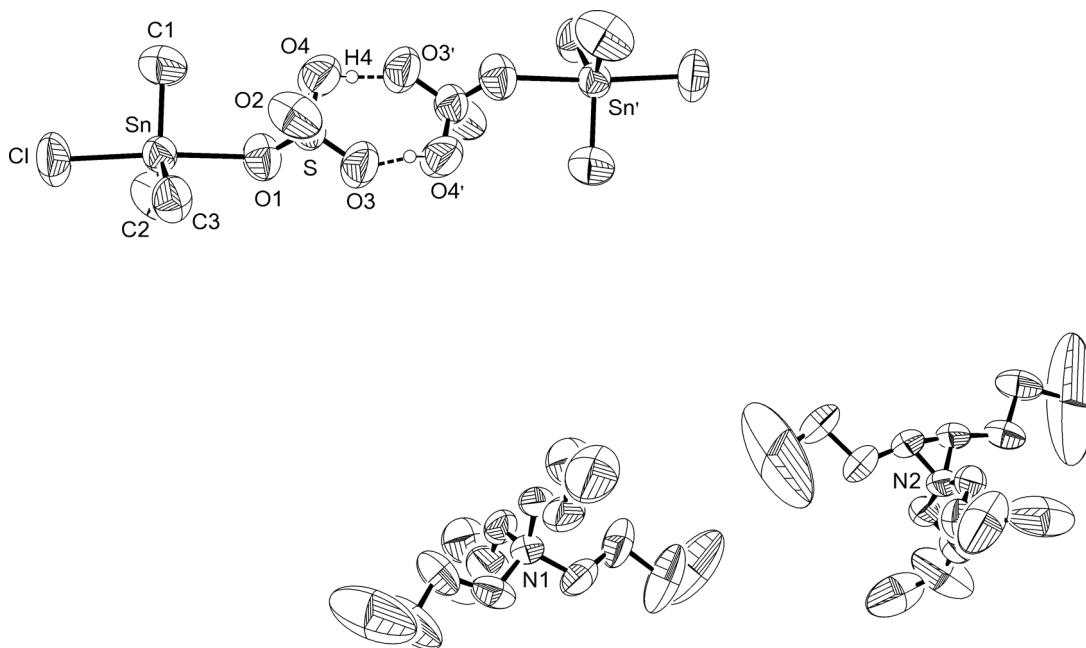


Figure 1. The asymmetric unit of (1) showing the labelling scheme used in the text and tables. (H atoms are omitted for clarity)

Symmetry transformation used to generate equivalent atoms: $-x, y, 1-z$.

CONCLUSION

The reported structure is the first example of SnMe₃Cl adduct with an oxyanion and also the first one containing HSO₄⁻, the anion being held in a dimeric acetic hydrogen bonding type.

Crystallographic data for the structure analysis has been deposited with Cambridge Crystallographic Data Center CCDC N° CCDC 670038. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge. Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

REFERENCES

1. Rheingold, A.L., Ng, S.W., Zuckermann, J.J.: *Organometallics*, **1984**, 3, 233;
2. Zoufala, P., Gyepes, R., Stepnicka, P.: *J. Organomet. Chem.*, **2004**, 689, 3556;
3. Teoh, S.G., Teo, S.B., Yeap, G.Y., Fun, H.K., Smith, P.J.: *J. Organomet. Chem.*, **1993**, 454, 73;
4. Denmark, S.E., Su, X.: *Tetrahedron*, **1999**, 55, 8727;
5. Teoh, S.G., Yeap, G.Y., Teo, S.B., Fun, H.K.: *Polyhedron*, **1995**, 14, 1051;
6. Courtenay, S., Ong C.M., Stephan, D.W.: *Organomet.*, **2003**, 22, 818;
7. Nikifirov, G.B., Roesky, H.W., Magull, J., Noltemeyer, M., Schmidt, H.G., Liyin, E.G., Kokunov Y.B., Demsar, A.: *Eur. J. Inorg. Chem.*, **2003**, 437;
8. Diassé-Sarr, A., Diop, L., Mahon, M.F., Molloy, K.C.: *Main Group Met. Chem.*, **1997**, 20 (4), 223;
9. Zang, D., Walz, L., Prager, M., Weiss, A.: *Ber. Bunsenges. Phys. Chem.*, **1987**, 91, 1283;
10. Molloy, K.C., Quill, K.C., Cunningham, D.C., Mc Ardle, P., Higgins, T.: *J. Chem. Soc. Dalton Trans.*, **1989**, 267
11. Diop, L., Mahon, M., Molloy, K.C., Sidibé, M.: *Main Group Met. Chem.*, **1997**, 20 (10), 649;
12. Diop, C.A.K., Toure, A., Diop, A., Bassene, S., Sidibe, M., Diop, L., Mahon, M.F., Molloy, K.C., Russo, U.: *J. Soc. Ovest. Afr. Chim.*, **2007**, 23, 49;
13. Goypiro, A., De Villepin, J., Novak, A.: *J. Raman Spectrosc.*, **1980**, 9 (5), 297;
14. Lahlou, M., Diop, L.: *Spectrochim. Acta*, **1991**, 47A (12), 1775;
15. Guèye, O., Qamar, H., Diop, L., Diop, C.A., Russo, U.: *Polyhedron*, **1993**, 12, 1245;
16. (a) Sheldrick, G.M.: *SHELXS-86: A Computer Program for Crystal Structure Determination*, University of Göttingen, Göttingen, **1986**; (b) Sheldrick, G.M.: *SHELXL-97: program for crystal structure refinement*, University of Göttingen, Göttingen, **1997**.
17. Nakamoto, K.: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., John Wiley and Sons, **1986**;
18. Bancroft, G.M., Platt, R.H.: Mossbauer spectra of inorganic compounds: Structure and bonding, in: *Advanced Inorganic Chemistry and Radiochemistry*, vol 15, (Emeleus, H.T., Sharpe, A.G. – editors), Academic Press, New York, **1972**.