

Full paper / Mémoire

Spectroscopic studies and crystal structure of tetrabutylammonium trichlorodimethylstannate(IV): $\text{Bu}_4\text{NSnMe}_2\text{Cl}_3$

Aminata Diasse-Sarr^{a,*}, Aliou Hamady Barry^a, Libasse Diop^a,
Ruben Alfredo Toscano^b, Bernard Mahieu^c

^a *Laboratoire de chimie minérale et analytique (LACHIMIA), département de chimie, faculté des sciences et techniques, université Cheikh-Anta-Diop de Dakar, Dakar, Sénégal*

^b *Instituto de Quimica, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México D.F. 04510, México*

^c *Département de chimie, CPMC, place Louis-Pasteur, B-1348 Louvain-la-Neuve, Belgique*

Received 29 September 2006; accepted after revision 19 December 2006

Available online 6 March 2007

Abstract

The structure of $\text{Bu}_4\text{NSnMe}_2\text{Cl}_3$ is found to be monomer, containing a 5-coordinated bipyramidal trigonal tin(IV) center. Crystals belong to the monoclinic space group $C2/c$, with unit-cell dimensions $a = 26.633(4) \text{ \AA}$; $b = 9.880(2) \text{ \AA}$; $c = 21.510(2) \text{ \AA}$; $\beta = 114.82(2)^\circ$; $Z = 8$; $D = 1.287 \text{ Mg/m}^3$; R is refined to 0.0537 and $R_w = 0.0642$ for 3330 reflections ($F > 2\sigma(F)$). **To cite this article:** A. Diasse-Sarr et al., *C. R. Chimie* 10 (2007).

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Résumé

La structure de $\text{Bu}_4\text{NSnMe}_2\text{Cl}_3$ est discrète et contient un atome d'étain pentacoordiné dans un environnement bipyramidal trigonal. $\text{Bu}_4\text{NSnMe}_2\text{Cl}_3$ cristallise dans le système monoclinique, groupe d'espace $C2/c$, les dimensions de la maille élémentaire étant $a = 26,633(4) \text{ \AA}$, $b = 9,880(2) \text{ \AA}$, $c = 21,510(2) \text{ \AA}$; $\beta = 114,82(2)^\circ$; $Z = 8$; $D = 1,287 \text{ Mg/m}^3$; R mesuré 0.0537 et $R_w = 0.0642$ pour 3330 réflexions ($F > 2\sigma(F)$). **Pour citer cet article :** A. Diasse-Sarr et al., *C. R. Chimie* 10 (2007).

© 2007 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Keywords: Trichlorodimethylstannate(IV); Crystal structure; Infrared; Mössbauer spectroscopy; NMR spectroscopy

Mots-clés : Trichlorodimethylstannate(IV) ; Structure cristallographique ; Spectroscopies infrarouge ; Spectroscopie mössbauer ; Spectroscopie RMN

1. Introduction

Organotin halogeno-species have already been extensively studied by both vibrational spectroscopy and X-ray diffraction [1–4]. The crystal structure of

* Corresponding author.

E-mail address: diasseam@yahoo.fr (A. Diasse-Sarr).

(Me₂SnCl, terpyridyl)⁺(Me₂SnCl₃)⁻ has also been reported by Einstein and Penfold [5], while the dimethyltin trichloride anion with tetraethylammonium as counter cation has been reported by Debye et al. [6]. While studying the interactions between the tetrabutylammonium hydrogenosulphate and dimethyltin dichloride, Bu₄N⁺SnMe₂Cl₃⁻ has been isolated. We report here the X-ray structure of Bu₄N⁺SnMe₂Cl₃⁻ to examine the influence of the cation.

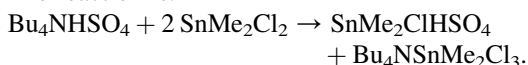
2. Experimental

2.1. Synthesis

Ethanol solutions containing Bu₄NHSO₄ (1.54 g; 9 mmol) and SnMe₂Cl₂ (0.99 g; 9 mmol) have been mixed and stirred at room temperature for more than 1 h.

After removing the precipitate, the filtrate was allowed to evaporate to give colourless crystals of the title compound. Analytical data: % found (% calculated): %C: 43.40 (43.50); %H: 8.37 (8.35); %N: 2.81 (2.79); %Cl: 21.40 (21.60); %Sn: 23.85 (23.90) [171° dec., yield 80%].

The reaction is:



The elemental analyses were performed by the ‘Service central d’analyses’, CNRS, Vernaison, France.

2.2. Infrared and Raman data (cm⁻¹)

The IR and Raman spectra were obtained as described in [7a] and [7b], respectively.

569s (526w) ν_{as} SnC₂; 515m (516vs) ν_s SnC₂; 316m (320m) ν_s SnCl₃; 240m (262w) ν_{as} SnCl₃ (the values in parentheses are related to the Raman spectrum).

2.3. Mössbauer data (mm s⁻¹)

The Mössbauer data are obtained as described in [8]. I.S. = 1.39; Q.S. = 3.56; Γ = 0.94.

2.4. NMR data [CDCl₃; δ (ppm); J (Hz)]

The NMR spectra were recorded in chloroform at the ‘Centre régional des mesures physiques de l’Ouest’, Rennes, France.

¹H: 1.02(t) (12H) –CH₂–CH₃; 1.36(q) (6H) SnMe₂; 1.44(m) (8H) N–CH₂; 1.65(m) (8H) CH₂–CH₂–CH₂; 3.24(m) (8H) CH₂–CH₂–CH₃; ²J_{Sn–H} = 84.5; 88.5

Table 1

Crystal data, data collection, solution and structure refinement for the title compound

Empirical formula	C ₁₈ H ₄₂ Cl ₃ NSn
Colour, habit	Colourless, irregular
Crystal size (mm)	0.68 × 0.60 × 0.36
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	<i>a</i> = 26.633(2) Å <i>b</i> = 9.880(2) Å, β = 114.82(2)° <i>c</i> = 21.510(2) Å
Volume	5137.0(7) Å ³
Z	8
Formula weight	497.6
Density (calc.)	1.287 Mg/m ³
Absorption coefficient	1.3087 mm ⁻¹
<i>F</i> (000)	2064
Diffractometer used	Siemens P4/PC
Radiation	Mo Kα (λ = 0.71073 Å)
Temperature (K)	293
Monochromator	Highly oriented graphite crystal
2θ Range	3.0°–55.0°
Scan type	ω/2θ
Scan speed	Variable; 4.00°–511.00° in ω
Scan width (ω)	0.78°
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
Standard reflections	3 Measured every 97 reflections
Index ranges	0 < <i>h</i> < 34, 0 < <i>k</i> < 12, –27 < <i>l</i> < 25
Reflections collected	6026
Independent reflections	5900 (<i>R</i> _{int} = 2.69%)
Observed reflections	3330 [<i>F</i> > 4.0σ(<i>F</i>)]
Absorption correction	Semi-empirical [9]
Min./max. transmission	0.2324/0.2982
System used	Siemens SHELXTL PLUS (PC version) [10]
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	∑w(<i>F</i> ₀ – <i>F</i> _c) ²
Absolute structure	N/A
Extinction correction	<i>X</i> = 0.00003(2), where <i>F</i> * = <i>F</i> [1 + 0.0008 <i>F</i> ² /sin(2θ)] ^{-1/4}
Hydrogen atoms	Riding model, fixed isotopic <i>U</i>
Weighting scheme	<i>w</i> ⁻¹ = σ ² (<i>F</i>) + 0.0008 <i>F</i> ²
Number of parameters refined	209
Final <i>R</i> indices (obs. data)	<i>R</i> = 5.37% , <i>wR</i> = 6.42%
<i>R</i> Indices (all data)	<i>R</i> = 9.62% , <i>wR</i> = 7.68%
Goodness-of-fit	1.27
Largest difference peak	0.93 eÅ ⁻³
Largest difference hole	–0.68 eÅ ⁻³
Deposit number (CCDC)	140722

Table 2
Selected bond lengths [Å] and angles [°]

Sn(1)—Cl(1)	2.563(2)	Sn(1)—Cl(2)	2.560(2)
Sn(1)—Cl(3)	2.387(3)	Sn(1)—C(1')	2.104(10)
Sn(1)—C(2')	2.110(11)	N(1)—C(1)	1.520(10)
N(1)—C(5)	1.523(9)	N(1)—C(9)	1.528(9)
N(1)—C(13)	1.506(7)	C(1)—C(2)	1.514(9)
C(2)—C(3)	1.509(12)	C(3)—C(4)	1.496(12)
C(5)—C(6)	1.498(9)	C(6)—C(7)	1.521(14)
C(7)—C(8)	1.479(13)	C(9)—C(10)	1.508(11)
C(10)—C(11)	1.540(14)	C(11)—C(12)	1.496(16)
C(14)—C(13)	1.507(11)	C(14)—C(15)	1.518(11)
C(15)—C(16)	1.515(13)		
Cl(1)—Sn(1)—Cl(2)	178.0(1)	Cl(1)—Sn(1)—Cl(3)	88.9(1)
Cl(2)—Sn(1)—Cl(3)	92.1(1)	Cl(1)—Sn(1)—C(1')	91.5(3)
Cl(2)—Sn(1)—C(1')	89.9(3)	Cl(3)—Sn(1)—C(1')	106.1(4)
Cl(1)—Sn(1)—C(2')	89.3(2)	Cl(2)—Sn(1)—C(2')	88.7(2)
Cl(3)—Sn(1)—C(2')	110.2(3)	C(1')—Sn(1)—C(2')	143.7(5)
C(1)—N(1)—C(5)	111.1(5)	C(1)—N(1)—C(9)	105.9(6)
C(5)—N(1)—C(9)	110.3(5)	C(1)—N(1)—C(13)	111.0(4)
C(5)—N(1)—C(13)	107.1(6)	C(9)—N(1)—C(13)	111.5(5)

Anisotropic thermal displacement coefficient, H-atomic coordinates and isotropic displacement coefficient can be obtained on request from authors.

^{13}C : 13.72(s) $-\text{CH}_2-\text{CH}_3$; 18.21(q) SnMe_2 ; 19.79(s) $\text{N}-\text{CH}_2$; 24.09(s) $\text{CH}_2-\text{CH}_2-\text{CH}_2$; 59.06(s) $\text{CH}_2-\text{CH}_2-\text{CH}_3$; ^{119}Sn : 712.10; 681.33
 ^{119}Sn : -100.94 .

2.5. Crystallography

X-ray-quality crystals were grown by slow evaporation of a methanol solution. A single crystal of approximate dimensions $0.68 \times 0.60 \times 0.36$ mm was used for data collection. Experimental details relating to the

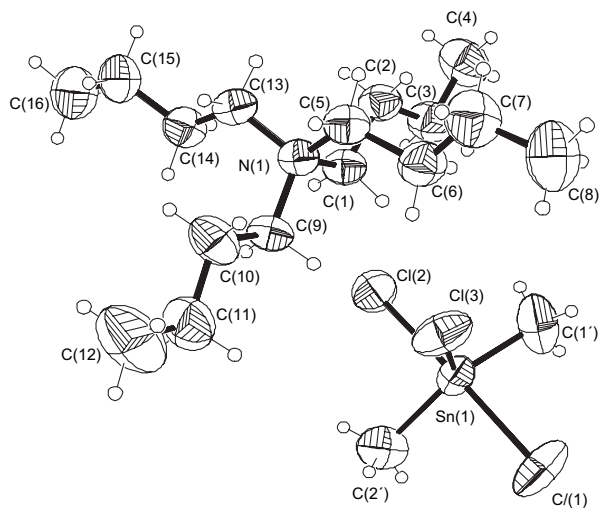


Fig. 1. ORTEP drawing of the title compound with the atomic numbering scheme.

crystal class, method of data collection and data manipulation are given in Table 1. Selected geometric data are given in Table 2.

The asymmetric unit used in text and tables is shown in Fig. 1.

3. Results and discussion

The presence of a band at 515 cm^{-1} due to $\nu_s \text{SnC}_2$ is indicative of a non-linear SnC_2 group [11]. The Q.S. value [Q.S. = 3.56 mm s^{-1}] is in the range of penta-coordinated tin centers [12].

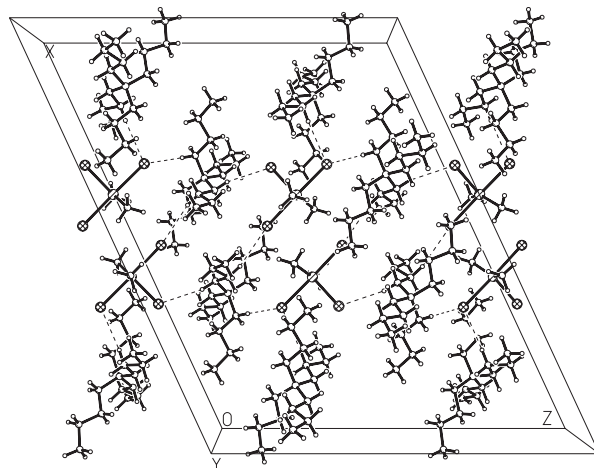


Fig. 2. The packing arrangement in the crystal.

The ^{119}Sn NMR exhibits one resonance at -100.94 ppm (in SnMe_2Cl_2 δ $^{119}\text{Sn} = 141$ ppm [13], the values of the coupling constants are $^1J_{\text{SnC}} = 712.1$; 681.3 Hz and $^2J_{\text{SnH}} = 84.5$; 88.5 Hz). The 2J value larger than 83 Hz is indicative of an SnC_2 angle above 135° [14].

Fig. 1 shows an ORTEP drawing of the asymmetric unit with the labelling scheme of the structure; Fig. 2 shows the packing arrangement in the crystal. It consists of an assemblage of Bu_4N^+ and $\text{SnMe}_2\text{Cl}_3^-$ entities, in which the tin atom adopts a trigonal bipyramidal environment with Cl(1) and Cl(2) in the axial positions and Cl(3), C(1') and C(2') in the equatorial positions. The axial SnCl bonds are almost collinear [$\text{Cl}(1)\text{—Sn—Cl}(2) = 178.0^\circ$]. The only important angular distortions from a regular trigonal bipyramidal configuration are within the equatorial plane. The angle between the methyl groups is 143.7° , while the two Me—Sn—Cl angles are 106.1° and 110.2° (the sum of the angles around the tin atom in the equatorial plane is 360°).

These results are in good agreement with those obtained in $(\text{Me}_2\text{SnCl, terpyridyl})^+(\text{Me}_2\text{SnCl}_3)^-$ [5]. In the latter case, the three equatorial planar angles are 140° , 107° and 113° , while the two axial Sn—Cl bonds are perfectly colinear [$\text{Cl—Sn—Cl} = 180^\circ$].

As it has been observed in $\text{Me}_2\text{SnCl}_3^-$ -containing compounds, the axial Sn—Cl bonds [$2.53(2)$ Å] are significantly greater than the equatorial one [$2.38(3)$ Å]; in $(\text{Me}_2\text{SnCl, terpyridyl})^+(\text{Me}_2\text{SnCl}_3)^-$ the distances are 2.54 and 2.32 Å, respectively. The Sn—C distances in the two compounds are also very similar: 2.10 Å in the present case and 2.11 Å in $(\text{Me}_2\text{SnCl, terpyridyl})^+(\text{Me}_2\text{SnCl}_3)^-$.

In the cation, the N—C and C—C distances are in the expected ranges [N—C: $1.506(7)$ – $1.528(9)$ Å; C—C: $1.479(13)$ – $1.540(14)$ Å], while the C—N—C angles deviate slightly from those in a regular tetrahedron [range: $105.9(6)^\circ$ – $111.1(5)^\circ$].

4. Conclusion

The structure of the title compound is discrete; the tin center adopts a trigonal bipyramidal environment,

as in the previously published compounds containing $\text{SnMe}_2\text{Cl}_3^-$ units: it appears that there is no cation effect on the environment of $\text{SnMe}_2\text{Cl}_3^-$, the interactions being essentially electrostatic.

Acknowledgements

The Dakar group thanks the Third World Academy of Sciences (TWAS) (Trieste – Italy) for financial support (Grant Number 93318 RG/AF/AC).

References

- [1] J.P. Clark, C.J. Wilkins, *J. Chem. Soc., A* (1966) 871.
- [2] I.R. Beattie, F.C. Stones, L.E. Alexander, *J. Chem. Soc., Dalton Trans.* (1973) 465.
- [3] G. Matsubayashi, K. Ueyama, T. Tanaka, *J. Chem. Soc., Dalton Trans.* (1985) 465.
- [4] J.S. Casas, A. Castineiras, M.D. Couce, G. Martinez, J. Sordo, J.M. Varela, *J. Organomet. Chem.* (1996) 165.
- [5] F.W. Einstein, B.R. Penfold, *J. Chem. Soc., A* (1968) 3019.
- [6] N.W.G. Debye, E. Rosenberg, J.J. Zuckerman, *J. Am. Chem. Soc.* 90 (1968) 3234.
- [7] [a] A.S. Sall, A. Diassé, O. Sarr, L. Diop, *Main Group Met. Chem.* 15 (1992) 265; [b] M. Sidibé, M. Lahlou, L. Diop, B. Mahieu, *Main Group Met. Chem.* 21 (10) (1998) 605.
- [8] M. Gielen, A. Bouhdid, F. Kayser, M. Biesemans, D. de Vos, B. Mahieu, R. Willem, *J. Organomet. Chem.* 9 (1995) 251.
- [9] N. Walker, D. Stuart, *Acta Crystallogr.* A39 (1938) 158.
- [10] G.M. Sheldrick, Siemens SHELXTL PLUS: Release 4.0 for Siemens R3 Crystallographic Research System, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1989.
- [11] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, fourth ed. John Wiley and Sons, 1986.
- [12] A.G. Davies, P.J. Smith, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 2, Pergamon Press, Oxford, UK, 1982 (Chapter 11).
- [13] [a] R.K. Harris, J.D. Kennedy, W. Mc Farlane, in: R.K. Harris, B.E. Mann (Eds.), *NMR and Periodic Table*, Academic Press, London, 1978, p. 342; [b] P.J. Smith, A.P. Tupciauskas, *Annu. Rev. NMR Spectrosc.* 8 (1978) 291.
- [14] T.P. Lockhart, F. Manders, *Inorg. Chem.* 25 (1986) 89.