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Journal of Organometallic Chemistry 601 (2000) 142–146

Journal of Organo metallic Chemistry

Synthesis and structural characterisation of bis(trimethylsilyl)amidotin(II) triflate $[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}OTf)_2\}]_\infty$ $(R = SiMe_3,\ ^-OTf = {}^-OSO_2CF_3)$

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Received 15 November 1999; accepted 24 November 1999

Dedicated to Professor S. Pasynkiewicz, as a mark of respect and friendship

Abstract

The amidotin(II) triflate $[\{Sn(NR_2)\{\mu\text{-}\eta^2\text{-}OTf)\}_2]_\infty$ (**1**) has been prepared in high yield by two methods: from $Sn(NR_2)_2 + HOTf$, or from $[Sn(NR_2)(\mu\text{-}Cl)]_2 + 2AgOTf$ $(R = SiMe_3,\ ^-OTf = {}^-OSO_2CF_3)$. The triflate ligand in the crystalline compound **1** binds to two tin atoms in an *O*,*O*′-bridging fashion (av. Sn–O 2.395(4) Å) and uses its third oxygen atom to bind more loosely to a tin atom of a neighbouring dinuclear tin unit [av. Sn–O″ 2.832(4) Å]. Multinuclear [^{1}H-, ^{13}C-, ^{19}F- and ^{119}Sn- (δ −78.0 in PhMe–C_6D_6 at 298 K)] NMR and ^{119}Sn Mössbauer (I.S. 3.37, Q.S. 3.75 mm s^{-1}) spectral data are reported. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Bis(trimethylsilyl)amide; Triflate; NMR and ^{119}Sn Mössbauer spectra; Crystallography

1. Introduction

This paper derives from complementary interests of two Sussex research groups, both of which have contributed to the chemistry of molecular compounds of divalent tin. Bulky amides, such as $^-N(SiMe_3)_2\{\equiv {}^-NR_2\}$ or $^-NC(Me)_2(CH_2)_3CMe_2$, have featured in the researches of the Lappert group (bulky amido ligands; for the most recent paper [on $\{N(CH_2Bu^t)\}_2C_{10}H_6$-1.8], see Ref. [1]), while novel cyclopentadienyls such as $[\eta^5\text{-}C_5Me_4(SiMe_2Bu^t)]^-$ have played an important role in Lawless' chemistry (for the most recent paper on the $[\eta^5\text{-}C_5Me_4(SiMe_2Bu^t)]^-$ ligand, see Ref. [2]). Earlier collaborations, which are relevant to the present paper, relate to (i) a study of *cis*/*trans* isomerism in the series of compounds $[Sn(NR'_2)(\mu\text{-}X)]_2$ [$R' = R$ or $NR'_2 = NC(Me)_2(CH_2)_3CMe_2$) and $X = Cl$ or Br] [3]; and (ii) a novel high-yield route to organic derivatives of the heavier Group 2 metals, based on the nucleophilic displacement of a triflate ligand $[\bar{O}SO_2CF_3]$ $(\equiv\bar{O}Tf)$ from $M(OTf)_2$ (M = Ca, Sr or Ba) and the molecular structure of $[\{Ba(OTf)_2\}_4(py)_{14}]\cdot py$ [4].

The triflate moiety has long been employed as an excellent leaving group in organic nucleophilic displacement reactions [5]. It provides good thermal stability and often lipophilicity in the substrate (not being a source of fluoride ions), is resistant to oxidative or reductive cleavage, and does not (even as HOTf) act as an oxidising agent. Increasingly it is also finding a similar niche in inorganic systems: as in the synthesis of Group 2 metal amides $M(NR_2)_2$ from $M(OTf)_2$ [4], or of $[\{Ln(\eta^5\text{-}C_5H_5)_2(OTf)\}_2]$ from $Ln(OTf)_3$ and $2Na(C_5H_5)$ (Ln = Sc or La) [6]. The chemistry of metal-coordinated triflate (trifluoromethanesulfonate) has been reviewed [7]. A noteworthy feature is the diversity of bonding modes adopted by metal triflates, ranging from the ionic (a), to the mono-, bi- or tridentate, terminal or bridging (b–f). In crystalline,

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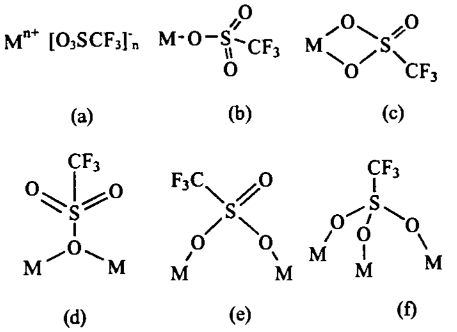
PII: S0022-328X(00)00048-6

$[\{Ba(OTf)_2)_4(py)_{14}]\cdot py$, three of these (c, e and f) coexist [4]. Tin(II) triflate, a non-volatile solid, insoluble in organic solvents has been assigned the ionic structure (a), on the basis of IR and Mössbauer spectroscopic data [8].



2. Results and discussion

2.1. Synthesis and characterisation of bis(trimethylsilyl)amidotin(II) triflate (1)

Treatment of the orange bis[bis(trimethylsilyl)amido]tin(II) compound, $Sn(NR_2)_2$ ($R = SiMe_3$) [9,10], with an equivalent portion of triflic acid, HOTf, in toluene at 0°C led to a discharge of colour. The colourless crystalline compound **1** (Eq. (1)) was obtained in good yield after removal of solvent, extracting the residue into hot hexane and concentrating and cooling the extract.

$$2Sn(NR_2)_2 + 2HOTf \xrightarrow{PhMe,\ 0°C} 1/_{\infty}[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}\overline{OTf})\}_2]_{\infty} + 2HNR_2 \quad (1)$$

1, 90%

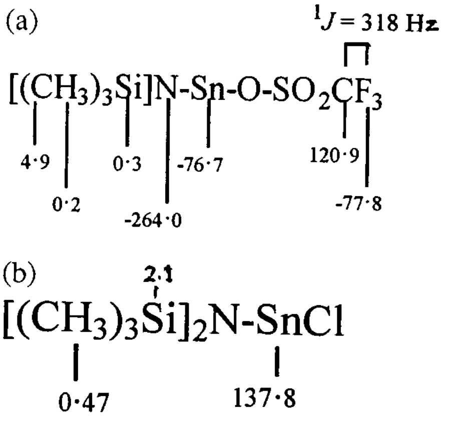


Fig. 1. (a) NMR spectral chemical shifts (δ) in C_6D_6 at 298 K for complex **1**: ^1H (400.13 MHz), $^{13}C\{^1H\}$ (100.61 MHz), $^{14}N\{^1H\}$ (28.91 MHz), $^{19}F\{^1H\}$ (376.5 MHz), $^{29}Si\{^1H\}$ (79.49 MHz) and $^{119}Sn\{^1H\}$ (149.21 MHz); δ [$^{119}Sn\{^1H\}$] −270 in C_4D_8O at 298 K. (b) NMR spectral chemical shifts (δ) in C_6D_6 at 298 K for complex **2**: ^1H (400.13 MHz), $^{29}Si\{^1H\}$ (79.49 MHz) and $^{119}Sn\{^1H\}$ (149.21 MHz); δ [$^{119}Sn\{^1H\}$] +39 in tetrahydrofuran with C_7D_8 as lock at 291 K.

Complex **1** was also prepared in good yield (Eq. (2)) by slow addition of solid silver triflate to an equivalent portion of bis(trimethylsilyl)amidotin(II) chloride, $[Sn(NR_2)(\mu\text{-}Cl)_2$ [9], in diethyl ether at ambient temperature. A colourless, free-flowing powder was produced after successively filtering and removing volatiles from the filtrate. The residue was extracted into hot hexane; concentration and cooling of the extract yielded colourless crystals of the amidotin(II) triflate **1**.

$$[Sn(NR_2)(\mu\text{-}Cl)]_2 + AgOTf \xrightarrow{Et_2O,\ 25°C} 1/_{\infty}[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}\overline{OTf})\}_2]_{\infty} + 2AgCl \quad (2)$$

1, 75%

Complex **1** was moderately soluble in hydrocarbons. It was air sensitive, but thermally stable, m.p. 116–119°C. It was characterised by (i) satisfactory elemental (C, H, N) analysis; (ii) the mass spectrum; (iii) multinuclear ^1H-, $^{13}C\{^1H)$-, $^{14}N(^1H\}$-, $^{19}F\{^1H\}$-, $^{29}Si\{^1H\}$- and $^{119}Sn\{^1H\}$-NMR spectra in benzene-d_6 at ambient temperature; (iv) the ^{119}Sn Mössbauer spectrum; and (v) a single-crystal X-ray diffraction study.

The EI mass spectrum of **1** at 70 eV showed the highest m/z fragment at 414 mass units, corresponding to $[Sn(NR_2)(OTf)\text{–}CH_3]^+$, at 14% intensity.

The ^1H-, $^{13}C\{^1H\}$-, $^{14}N\{^1H\}$-, $^{19}F\{^1H\}$-, $^{29}Si\{^1H\}$- and $^{119}Sn\{^1H\}$-NMR spectral chemical shifts in benzene-d_6 at 298 K are summarised in Fig. 1(a). The $^{13}C\{^1H\}$- and $^{19}F\{^1H\}$-NMR spectra both revealed a coupling constant of 318 Hz between the ^{13}C and ^{119}F nuclei, with $\delta(^{13}C) = 120.9$ and $\delta(^{19}F) = -77.8$ for the CF_3 moiety; these data are closely similar to those recorded for the anhydrous alkaline earth metal triflates $M(OTf)_2$ in pyridine/pyridine-d_5: $\delta(^{13}C) = 121.2 \pm 0.2$, $\delta(^{19}F) = -78$ and $^1J(^{13}C\text{–}^{19}F) = 319.1 \pm 0.3$ Hz (M = Ca, Sr or Ba) [4]. The other NMR spectral data for **1**, except for $^{119}Sn\{^1H)$, are unexceptional, as evident from comparison with similar results on $[Sn(NR_2)(\mu\text{-}Cl)]_2$, (**2**) Fig. 1(b), ($^1H$ data on **2** have previously been reported [3]). Compounds **1** and **2** are rare examples of crystalline dinuclear complexes $[\{Sn(NR_2)(\mu\text{-}X)\}_2]$.

The $^{119}Sn\{^1H\}$ spectrum of **1** in C_6D_6 at 298 K showed a singlet at δ −77.8 or δ −75.0 in toluene-d_8, but at δ −270 in tetrahydrofuran-d_8. These chemical shifts are in the range expected for tin(II) compounds; cf. δ −137.8 for **2** in C_6D_6, δ +39 in C_4D_8O [3] and δ −12 for the three-coordinate tin nuclei in μ-Sn[{μ-$O_2C_6H_3Bu^t_2$-3,5)Sn(NR_2)]_2$ [11]. The $^{119}Sn\{^1H\}$-NMR spectrum of **1** at 243 K in toluene-d_8 showed a singlet at δ −99 and δ −121 at 218 K; efforts to extend this variable temperature range downwards were hampered by solubility problems. Hence, it was not possible the determine the existence of *cis* and *trans* forms of **1**, which could rapidly exchange down to < 243 K; similar studies on $[Sn(\mu\text{-}Cl)\text{-}\{\overline{NCMe_2(CH_2)_3CMe_2}\}]_2$ showed the existence below 192 K of *cis* and *trans* isomers [3]. The change in solvent from toluene to THF for both **1** and **2** resulted in a substantial shift to a lower frequency in the ^{119}Sn-NMR spectral chemical shift, consistent with the notion that in THF both **1** and **2** are mononuclear, but dinuclear in toluene. It is likely, that in THF **1** is a tight ion pair whereas **2** is probably covalent, $Sn(NR_2)(Cl)(THF)_n$.

^{119}Sn Mössbauer spectroscopic examination of complex **1** revealed parameters in accordance with the tin(II) formulation: I.S. = 3.37 mm s^{-1} and Q.S. = 3.75 mm s^{-1}. The high value of Q.S. and the asymmetry in the absorption lines are indicative of strong intermolecular interactions in the solid state. These parameters differ substantially from values for $Sn(OTf)_2$ which displayed I.S. values greater than 4.0 mm s^{-1}, appropriate for highly ionic lattices [8]; however, the data are not too far remote from those for $[Sn(NR_2)(\mu\text{-}Cl)]_2$ (**2**): I.S. = 3.28 mm s^{-1}, Q.S. = 3.10 mm s^{-1}, which we have determined for comparison.

The molecular structure of the crystalline complex **1** with the atom labelling is illustrated in Fig. 2. Selected bond lengths and angles are listed in Table 1. Complex **1** comprises dinuclear units, the two tin atoms being bridged by a bidentade triflate ligand, Sn(1)–O(2) 2.489(4), Sn(1)–O(5) 2.324(4) Å [Sn(2)–O(6) 2.476(4), Sn(2)–O(3) 2.291(4) Å]. The bis(trimethylsilyl)amido ($\overline{N}R_2$) terminal ligands are *trans* to one another, as in the crystalline complex **2** [3]. Each tin atom in **1** may be regarded as being at the centre of a distorted trigonal bipyramid, with the lone pair of electrons occupying an apical site. The coordination number of four for each tin atom is completed by a longer intermolecular Sn···O contact to a neighbouring binuclear unit, Sn(1)–O(1)′ 2.794(4), Sn(2)–O(4)″ 2.870(5) Å. This high degree of association is consistent with a strongly ionic lattice. The geometric parameters of the R_2N–Sn moiety of **1** (Fig. 3(A)) is unexceptional, as evident from comparison with the same fragment in the crystalline complex **2**, Fig. 3(B) [3].

Some NMR spectral experiments were carried out. These involved adding pyridine, 2,2′-bipyridine or 2,4,6-tri-*t*-butylphenol to **1** in toluene-d_8. Addition of either of the neutral bases resulted in an immediate development of the orange colour of $Sn(NR_2)_2$, as confirmed by the $^{119}Sn\{^1H\}$-NMR spectrum, showing a singlet at δ 776 [9]. The phenol reaction afforded a compound believed to be $Sn(OC_6H_2Bu^t_3\text{-}2,4,6)(OTf)$, δ [$^{119}Sn\{^1H\}$] -189 {MS = m/z 530 $[M]^+$ and 381 $[M-OTf]^+$}.

3. Experimental

3.1. Materials and procedures

All manipulations were carried out under vacuum or argon by Schlenk techniques, or using a glove box under an atmosphere of nitrogen gas (< 1 ppm H_2O or O_2). Solvents were dried and distilled from sodium–potassium alloy under argon or nitrogen gas prior to use. The following compounds were prepared by known procedures: $Sn(NR_2)_2$ [9] and $[Sn(NR_2)(\mu\text{-}Cl]_2$ [3,10]. Microanalyses were carried out by Medac Ltd. (Brunel University). Solution-state NMR spectra were recorded at 400.13 MHz (^{1}H), 100.13 MHz (^{13}C), 28.91 MHz (^{14}N), 376.5 MHz (^{19}F), 76.49 MHz (^{29}Si) and 149.21 MHz (^{119}Sn) using a Bruker DMX-400 spectrometer. The melting point was determined in a sealed capillary under an argon atmosphere and is uncorrected. The mass spectra were recorded on a VG Autospec instrument operating in the EI mode at 70 eV. The ^{119}Sn Mössbauer spectral measurements were made under the supervision of Dr B. Mahieu at the Université Catholique de Louvain, Belgium; measurements were carried out at liquid-nitrogen temperature using a $Ca^{119}SnO_3$ source.

3.2. Synthesis of $[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}\overline{OTf_2)\}]}_\infty$ (1)

Triflic acid (1.11 g, 7.4 mmol) was added by syringe over a 5 min period to a stirred solution of bis[-bis(trimethylsilyl)amido]tin(II) (3.25 g, 7.4 mmol) in toluene (70 ml) in a Schlenk tube at 0°C, with stirring. After 15 min, the orange colour had disappeared. The mixture was allowed to warm to ambient temperature and stirring was continued for a further 1 h. Volatiles were removed under vacuum and the residue was extracted with hot hexane (50 ml). Removal of the volatiles under vacuum afforded the white powder **1** (2.85 g, 90%). Anal. Calc. for $C_{14}H_{36}F_6O_6S_2Si_4Sn_2$: C, 19.6; H, 4.24; N, 3.27. Found: C, 19.0; H, 3.97; N, 3.25%.

Silver triflate (2.3 g, 8.8 mmol) was added in portions to a stirring solution of $[Sn(NR_2)(\mu\text{-}Cl)]_2$ (2.8 g, 4.4 mmol) in diethyl ether (100 ml) at ambient temperature. The brown reaction mixture was stirred for 18 h in the absence of light. A small quantity of brown precipitate was filtered off under vacuum, yielding a free-flowing white powder, which was extracted into boiling hexane (50 ml). The extract was filtered; the filtrate was set aside for 24 h at ambient temperature to give colourless crystals of **1** (2.8 g, 75%).

3.3. X-ray structure determination of the crystalline complex 1

X-ray quality single crystals of **1** were obtained by recrystallisation from hexane. Data were measured on

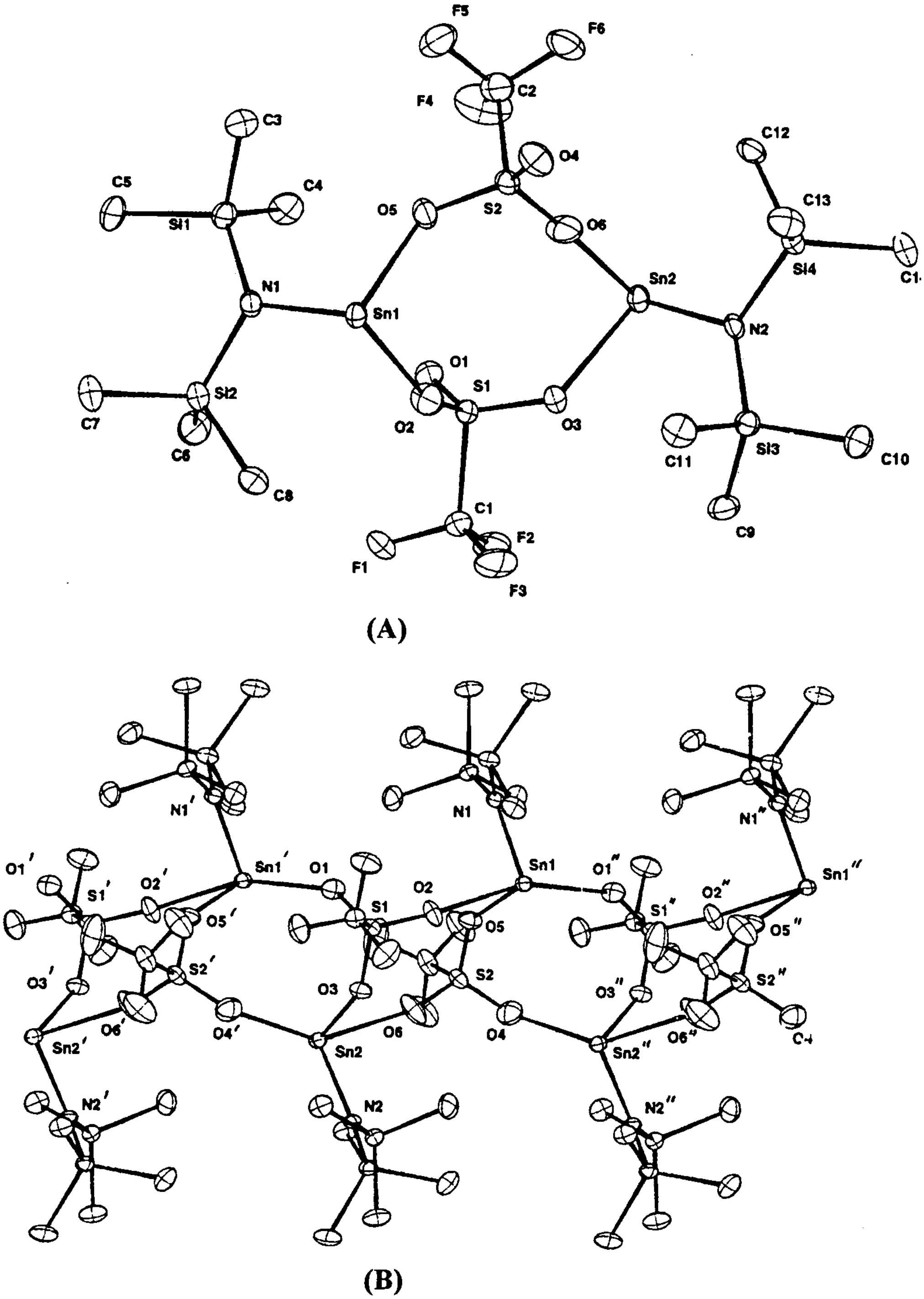


Fig. 2. (A) The molecular structure of $[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}OSO_2CF_3)\}_2]$ (**1**) and atom numbering scheme; (B) the unit cell of **1**.

an Enraf–Nonius CAD4 diffractometer using monochromated Mo–K_α radiation. The crystal of **1** was enclosed in an oil drop and frozen in a stream of cold nitrogen gas. Corrections for absorption were made using ψ-scans. The structure was refined on F^2 using SHELXL-93 [12]. Further details are given in Table 2. Tables of atom positions and thermal parameters have been deposited at CCDC. All non-H atoms were anisotropic; hydrogen atoms were included in a riding mode. A difference map revealed a poorly defined hexane solvate molecule lying across an inversion centre; this was included with isotropic C atoms and C–C bond lengths constrained to be equal, with H atoms omitted.

Table 1
Selected bond lengths (Å) and angles (°) for **1** [a]

Bond lengths			
Sn(1)–N(1)	2.047(4)	Sn(1)–O(5)	2.324(4)
Sn(1)–O(2)	2.489(4)	Sn(1)–O(1)′	2.794(4)
Sn(2)–N(2)	2.041(4)	Sn(2)–O(3)	2.291(4)
Sn(2)–O(6)	2.476(4)	Sn(2)–O(4)″	2.870(5)
Bond angles			
N(1)–Sn(1)–O(5)	93.5(2)	N(1)–Sn(1)–O(2)	93.0(2)
O(5)–Sn(1)–O(2)	79.09(14)	N(1)–Sn(1)–O(1)′	101.9(2)
O(5)–Sn(1)–O(1)′	80.94(13)	O(2)–Sn(1)–O(1)′	155.74(12)
N(2)–Sn(2)–O(3)	93.8(2)	N(2)–Sn(2)–O(6)	90.7(2)
O(3)–Sn(2)–O(6)	76.08(14)	N(2)–Sn(2)–O(4)″	107.46(14)
O(3)–Sn(2)–O(4)″	71.09(13)	O(6)–Sn(2)–O(4)″	143.18(14)

[a] Symmetry transformations used to generate equivalent atoms: ′ $x, -y+1/2, z+1/2$, ″ $x, -y+1/2, z-1/2$.

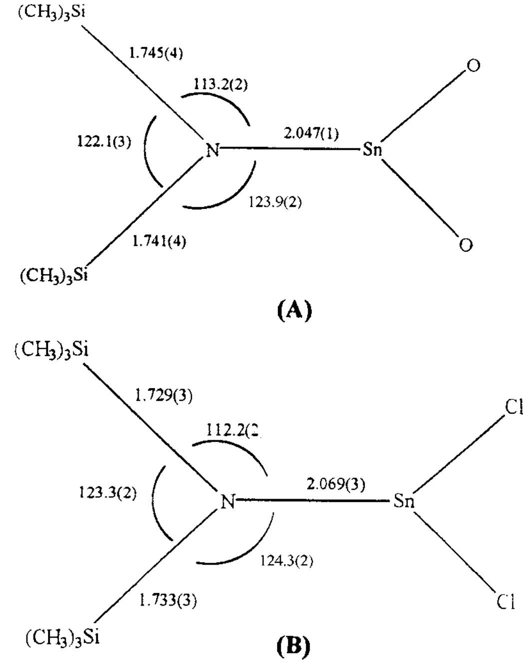


Fig. 3. (A) Selected geometric parameters for the R_2N–Sn fragment of **1**. (B) Selected geometric parameters for the R_2N–Sn fragment of **2**.

4. Supplementary material

Crystallographic data for the structural analysis of complex **1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 139260). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 2
X-ray crystal data and structure refinement for **1**

Compound	**1**
Empirical formula	$C_{14}H_{36}F_6N_2O_6S_2Si_4Sn_2$
Formula weight	856.3
Temperature (K)	173(2)
Wavelength	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	
a (Å)	16.174(5)
b (Å)	17.409(5)
c (Å)	12.856(2)
β (°)	112.97(2)
Volume (Å^3)	3333(2)
Z	4
Absorption coefficient (mm^{-1})	1.83
θ Range for data collection (°)	2–25
Reflections collected	6118
Independent reflections	5851 [$R_{int} = 0.0358$]
Reflections with $I > 2\sigma(I)$	4671
Refinement method	Full-matrix least-squares on all F^2
Data/restraints/parameters	5850/0/325
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.088$
R indices (all data)	$R_1 = 0.054$, $wR_2 = 0.097$

Acknowledgements

We thank the Brazilian Government (Ministério de Ciência e Tecnologia, CNPq) for a grant for G.deL., the European Commission for a category 20 TMR grant for L.J.-M.P., EPSRC for other support and Dr B. Mahieu for supervising the Mössbauer spectral measurements.

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