APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 204–212

Diethyl- and dibutyltin dihalide complexes of 1-methyl-2(3*H*)-imidazolinethione: synthesis, structure and antibacterial activity

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The compounds $[SnR_2X_2(Hmimt)]$ (R = Et, Bu; X = Cl, Br; Hmimt = 1-methyl-2(3*H*)-imidazolinethione) and $[SnEt_2X_2(Hmimt)_2]$ (X = Cl, Br) have been prepared and characterized by elemental analysis, mass spectrometry and IR, Raman, Mössbauer and NMR (^1H, ^{13}C and ^{119}Sn) spectroscopy. An X-ray study of the crystal structure of $[SnEt_2Cl_2(Hmimt)_2]$ shows all-*trans* octahedral stereochemistry with the tin atom coordinated to two ethyl carbon atoms, two chlorine atoms and the sulfur atoms of the two Hmimt ligands. Hmimt exhibits antibacterial activity against *Bacillus subtilis* (MIC = 6.25 μg ml^{-1}), and all the complexes inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* as well as *B. subtilis*, with MIC values of 12.5 μg ml^{-1}, 6.25 μg ml^{-1} and 3.12 μg ml^{-1} respectively, for the most active complex, $[SnBu_2Cl_2(Hmimt)]$. Only $[SnEt_2Cl_2(Hmimt)]$ shows activity against *Pseudomonas aeruginosa* (MIC = 50 μg ml^{-1}).

Keywords: tin; dialkyltin dihalide complexes; 1-methyl-2(3*H*)-imidazolinethione complexes; crystal structure; vibrational spectroscopy; Mössbauer spectroscopy; NMR spectroscopy; antibacterial activity

Received 17 May 2000; accepted 14 September 2000

INTRODUCTION

Sn—S bonds are featured by the complexes of organotin species with a number of biologically important thiols[1] and by several compounds with industrial[2] or pharmaceutical[3,4] applications. Accordingly, significant effort is being devoted to synthesizing organometallic compounds with Sn—S bonds and characterizing their structures.[5] In our work in this field we have previously[6] studied the structures of compounds of the types $[SnR_2Cl_2(Hmimt)]$ and $[SnR_2Cl_2(Hmimt)_2]$ prepared by reaction of the sulfur-donor ligand 1-methyl-2(3*H*)-imidazolinethione (Hmimt) with dimethyl- and diphenyltin dichlorides in CH_2Cl_2 {$[SnMe_2Cl_2(Hmimt)]$ and $[SnPh_2Cl_2(Hmimt)_2]$ were later prepared by Pettinari *et al.*[7] in diethyl ether}. We have now prepared compounds $[SnR_2X_2(Hmimt)]$ (R = Et, Bu; X = Cl, Br) and $[SnEt_2X_2(Hmimt)_2]$ (X = Cl, Br) and determined the crystal structure of $[SnEt_2Cl_2(Hmimt)_2]$; and since tin-bonded ethyl and butyl groups are biologically active (as is Hmimt, to a small extent[8]), we have characterized these compounds not only spectroscopically but also with regard to their antibacterial activities against *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*

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and *Bacillus subtilis*. The compounds described are all new except [$SnBu_2Cl_2$(Hmimt)], the crystal structure of which has been reported previously[9].

EXPERIMENTAL DETAILS

Materials and measurements

Diethyltin dichloride, diethyltin dibromide, dibutyltin dichloride and dibutyltin dibromide (all from Ventron and/or Aldrich) and Hmimt (from Ega-Chemie and Aldrich) were used as supplied. Solvents were purified by standard methods.

Analytical data were obtained with Carlo Erba 1108 and Perkin Elmer 240B apparatus, and melting points with Büchi equipment. Electron impact (EI) mass spectra (70 eV, 250 °C) were recorded on a Kratos MS50 TC spectrometer connected to a DS90 operating system; nominal values were calculated considering the isotopes ^{120}Sn, ^{79}Br and ^{35}Cl. The IR spectra of Nujol mulls or KBr pellets and the Raman spectra of polycrystalline samples were recorded on a Bruker IFS-66V spectrometer with a Raman FRA 106 accessory. Mössbauer spectra were recorded at 80.0 K in a Harwell cryostat; the $Ca^{119}SnO_3$ source (15 mCi, New England Nuclear) was moved at room temperature with constant acceleration, giving a triangular velocity waveform, and Lorentzian line shapes were fitted to the experimental data. The molar conductivities of 10^{-3} M acetonitrile solutions were measured with a WTW LF-3 conductivity meter. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker WM-250 and AMX-300 spectrometers; chemical shifts are stated relative to external $SiMe_4$ for ^1H and ^{13}C, and to $SnMe_4$ for ^{119}Sn.

Antibacterial activity

Four bacteria were employed: *E. coli* (ATCC 25922), *P. aeruginosa* (ATCC 27853), *S. aureus* (ATCC 292135) and *B. subtilis* (ATCC 6633). Antibacterial activity was initially assayed by Muller–Hinton agar diffusion methods. Discs of paper 5 mm in diameter were loaded with 20 µl of a 2 mg ml^{-1} solution of the product to be tested {Hmimt, SnR_2X_2 or [SnR_2X_2(Hmimt)$_n$] (n = 1, 2)} in 9:1 ethanol–water; control discs were loaded with solvent alone. The discs were placed on dishes of Muller–Hinton agar inoculated with *E. coli*, *P. aeruginosa*, *S. aureus* or *B. subtilis*, and after 24 h incubation at 37 °C the diameter of the zone of bacterial growth inhibition was measured. Minimum inhibitory concentrations (MICs) for those products which showed activity in the diffusion test were determined using serial dilutions in Muller–Hinton broth in microwell plates (200 µl of culture per well).

Synthesis

General procedure

The compounds were prepared by slow addition of a solution of the appropriate diorganotin(IV) dihalide (*ca* 20 ml) to *ca* 20 ml of a solution of Hmimt in the same solvent {dry benzene [**safety—caution**] for [$SnEt_2Cl_2$(Hmimt)], dry CH_2Cl_2 for all the other compounds}. The mixture was stirred for 4 days, the solvent was evaporated off, the oil or solid so obtained was stirred (the former) or washed (the latter) with dry benzene, and final filtration extracted a solid that was dried *in vacuo*.

[$SnEt_2Cl_2$(Hmimt)]

From 0.502 g of $SnEt_2Cl_2$ (2.03 mmol) and 0.231 g of Hmimt (2.03 mmol). Anal. Found: C, 26.5; H, 4.4; N, 7.8%. $C_8H_{16}Cl_2N_2SSn$ requires: C, 26.6; H, 4.5; N, 7.7%. M.p. 90 °C. Λ_M (MeCN, 10^{-3} M) 1.2 S cm^2mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 114 (Hmimt, 69.5), 120 (Sn, 26.7), 149 (SnEt, 13.8), 155 (SnCl, 100.0), 184 (SnEtCl, 26.1), 190 ($SnCl_2$, 17.8), 213 ($SnEt_2Cl$, 37.1), 219 ($SnEtCl_2$, 95.5), 233 (Sn + mimt, 4.9), 248 ($SnEt_2Cl_2$, 16.3), 268 (SnCl + mimt, 2.5), 297 (SnEtCl+mimt, 2.5). IR and Raman (in parentheses), cm^{-1}: 510w (510w), ν_{as}(Sn—C); 489m (492vs), ν_{sym}(Sn—C); 352m (351m), ν(Sn—S); 276sh (270sh), ν(Sn—Cl). Mössbauer spectrum (mm s^{-1}): δ 1.76; Δ 3.28; Γ 0.96.

[$SnEt_2Cl_2$(Hmimt)$_2$]

From 0.820 g of $SnEt_2Cl_2$ (3.31 mmol) and 0.756 g of Hmimt (6.62 mmol). Anal. Found: C, 30.0; H, 4.7; N, 11.8%. $C_{12}H_{22}Cl_2N_4S_2Sn$ requires: C, 30.3; H, 4.7; N, 11.8%. M.p. 100 °C. Λ_M (MeCN, 10^{-3} M) 1.0 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 81 (Hmimt-SH, 12.4), 114 (Hmimt, 100.0), 120 (Sn, 4.7), 155 (SnCl, 41.1), 184 (SnEtCl, 8.4), 190 ($SnCl_2$, 5.5), 213 ($SnEt_2Cl$, 12.4), 219 ($SnEtCl_2$, 46.0), 233 (Sn + mimt, 0.6), 248 ($SnEt_2Cl_2$, 10.6), 268 (SnCl + mimt, 1.7), 297 (SnEtCl + mimt, 1.8). IR and Raman (in parentheses), cm^{-1}: 518m (518w), ν_{as}(Sn—C); 466w (466vs), ν_{sym}(Sn—C); 231s,

195m (225w, 204m), *v*(Sn—Cl). Mössbauer spectrum (mm s^{-1}): δ 1.91; Δ 3.96; Γ 1.18.

[$SnEt_2Br_2$(Hmimt)]
From 0.754 g of $SnEt_2Br_2$ (2.24 mmol) and 0.256 g of Hmimt (2.24 mmol). Anal. Found: C, 21.7; H, 3.8; N, 6.6%. $C_8H_{16}Br_2N_2SSn$ requires: C, 21.3; H, 3.6; N, 6.2%. M.p. 105 °C. Λ_M (MeCN, 10^{-3} M) 2.9 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m*/*z* (ion, intensity): 81 (Hmimt-SH, 10.4), 114 (Hmimt, 100.0), 199 (SnBr, 3.1), 263 (SnEt + Hmimt, 0.4), 307 ($SnEtBr_2$, 5.0), 313 (SnBr + Hmimt, 0.9), 336 ($SnEt_2Br_2$, 0.4). IR and Raman (in parentheses), cm^{-1}: 515w (515w), ν_{as}(Sn—C); 485m (485vs), ν_{sym}(Sn—C); 349m (348m), *v*(Sn—S). Mössbauer spectrum (mm s^{-1}): δ 1.82; Δ 3.21; Γ 0.87.

[$SnEt_2Br_2$(Hmimt)$_2$]
From 0.814 g of $SnEt_2Br_2$ (2.42 mmol) and 0.552 g of Hmimt (4.84 mmol). Anal. Found: C, 25.8; H, 4.0; N, 10.2%. $C_{12}H_{22}Br_2N_4S_2Sn$ requires: C, 25.5; H, 3.9; N, 9.9%. M.p. 100 °C. Λ_M (MeCN, 10^{-3} M) 6.8 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m*/*z* (ion, intensity): 81 (Hmimt-SH, 14.8), 114 (Hmimt, 100.0), 120 (Sn, 9.2), 199 (SnBr, 52.2), 263 (SnEt + Hmimt, 8.7), 278 ($SnBr_2$, 7.0), 307 ($SnEtBr_2$, 60.5), 312 (SnBr + mimt, 1.0), 313 (SnBr + Hmimt, 10.0), 336 ($SnEt_2Br_2$, 5.3). IR and Raman (in parentheses), cm^{-1}: 517m (518w), ν_{as}(Sn—C); 460w (462vs), ν_{sym}(Sn—C). Mössbauer spectrum (mm s^{-1}): δ 1.97; Δ 3.91; Γ 1.14.

[$SnBu_2Cl_2$(Hmimt)]
From 0.466 g of $SnBu_2Cl_2$ (1.53 mmol) and 0.175 g of Hmimt (1.53 mmol). Anal. Found: C, 33.3; H, 6.2; N, 6.0%. $C_{12}H_{24}Cl_2N_2SSn$ requires: C, 34.5; H 5.8, N, 6.7%. M.p. 71 °C. Λ_M (MeCN, 10^{-3} M) 2.5 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m*/*z* (ion, intensity): 81 (Hmimt-SH, 10.1), 114 (Hmimt, 100.0), 120 (Sn, 8.3), 155 (SnCl, 63.4), 190 ($SnCl_2$, 5.2), 212 (SnBuCl, 47.5), 233 (Sn + mimt, 7.1), 247 ($SnBuCl_2$, 57.1), 325 (SnBuCl + mimt, 2.4). IR and Raman (in parentheses), cm^{-1}: (604m), ν_{sym}(Sn—C); 346m (345m), *v*(Sn—S); 260sh (259m), v(Sn—Cl). Mössbauer spectrum (mm s^{-1}): δ 1.75; Δ 3.22; Γ 0.90.

[$SnBu_2Br_2$(Hmimt)]
From 0.845 g of $SnBu_2Br_2$ (2.15 mmol) and 0.246 g of Hmimt (2.15 mmol). Anal. Found: C, 28.7; H, 5.0; N, 5.6%. $C_{12}H_{24}Br_2N_2SSn$ requires: C, 28.4; H, 4.8; N, 5.5%. M.p. 67 °C. Λ_M (MeCN, 10^{-3} M) 2.5 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m*/*z* (ion, intensity): 81 (Hmimt-SH, 8.7), 114 (Hmimt, 100.0), 199 (SnBr, 14.9), 233 (Sn + mimt, 1.9), 256 (SnBuBr, 4.8), 335 ($SnBuBr_2$, 22.4). IR and Raman (in parentheses), cm^{-1}: (600m), ν_{sym}(Sn—C); 345m (345m), *v*(Sn—S). Mössbauer spectrum (mm s^{-1}): δ 1.80; Δ 3.16; Γ 0.86.

Crystal structure determination

X-ray data collection and reduction

Crystals suitable for X-ray diffraction studies were obtained by diffusion of n-hexane into a solution of [$SnEt_2Cl_2$(Hmimt)$_2$] in benzene–chloroform. The X-ray diffraction pattern was recorded at room temperature on a Siemens CCD Smart apparatus using Mo Kα radiation (λ = 0.710 73 Å), and was corrected with SADABS (Siemens area detector absorption correction).[10] The crystal data, experimental details and refinement results are summarized in Table 1.

Structure solution and refinement

The crystal structure was solved by direct methods,[11] which revealed the positions of all the non-hydrogen atoms, and was refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for non-hydrogen atoms.[11] All the hydrogen atoms except one were assigned calculated positions that were refined using a rigid model; the exception (the hydrogen-bonding hydrogen on N2) was located from a difference Fourier map and refined isotropically. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*,[12] and graphics were produced using the programs ORTEPIII[13a] and PLUTO.[13b]

RESULTS AND DISCUSSION

Synthesis

The complexes [SnR_2X_2(Hmimt)] were prepared by reacting the appropriate diorganotin dihalide with Hmimt in 1:1 mole ratio in non-coordinanting solvent CH_2Cl_2, except that [$SnEt_2Cl_2$(Hmimt)] was prepared in dry benzene because the 1:1 reaction in CH_2Cl_2 afforded [$SnEt_2Cl_2$(Hmimt)$_2$], (Eqn [1]):

$$SnR_2X_2 + \text{Hmimt} \rightarrow [SnR_2X_2(\text{Hmimt})] \quad (R = Et, Bu;\ X = Cl, Br) \quad [1]$$

Table 1 Crystal, intensity and structure refinement data for $[SnEt_2Cl_2(Hmimt)_2]$

Empirical formula	$C_{12}H_{22}Cl_2N_4S_2Sn$
Formula weight	476.05
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system/space group	Monoclinic/$P2_1/n$
Unit cell dimensions	
a (Å)	9.6113(4)
b (Å)	10.0125(3)
c (Å)	10.0762(4)
β (°)	101.125(1)
Volume (Å^3)	951.44(6)
Z	2
Density (calculated) (Mg m^{-3})	1.662
Absorption coefficient (mm^{-1})	1.841
F(000)	476
Crystal size (mm)/Colour	0.10 × 0.25 × 0.30/colourless
θ range (°)	2.68 to 28.39
Index ranges	$-12 \le h \le 12$, $-10 \le k \le 13$, $-12 \le l \le 13$
Reflections collected	6235
Independent reflections	2371 (R_{int} = 0.0510)
Criterion for observation	$I > 2\sigma(I)$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2371/0/101
Goodness-of-fit on F^2	0.960
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0380, wR_2 = 0.0926
Largest diff. peak and hole (e· Å^{-3})	1.548 and −0.865

When the reactions were carried out in 1:2 mole ratio in CH_2Cl_2, the dibutyltin dihalides gave Hmimt solvates of the 1:1 complex {the elemental analyses corresponded to 1:2 complexes, but the Mössbauer and vibrational data clearly indicated non-coordination of the second Hmimt molecule; for example, for the chloro derivative δ = 1.79, Δ = 3.32, Γ = 1.17 and the diagnostic IR and/or Raman bands lie at 603m [R, ν_{sym}(Sn—C)], 346m [R = 345m, ν(Sn—S)] and 260sh [R = 259m, ν(Sn—Cl)]} (Eqn 2):

$$SnR_2X_2 + 2Hmimt \longrightarrow [SnR_2X_2(Hmimt)_2] \quad (R = Et; X = Cl, Br) \longrightarrow [SnR_2X_2(Hmimt)] \cdot Hmimt \quad (R = Bu; X = Cl, Br) \quad [2]$$

The non-formation of the 1:2 butyl complexes may be attributed to the relatively low acceptor capacity of the butyl derivatives[14] and the low basicity of the ligand. Even the 1:1 complex $SnBu_2Cl_2$ was not isolated when its synthesis was attempted in the weakly coordinating solvent diethyl ether.[7]

All the complexes have melting points below 105 °C and are soluble in the usual organic solvents. The absence of signals for the molecular ion in their mass spectra is attributable to fast fragmentation of these species under EI conditions and/or to their thermal decomposition. The presence of an intense Hmimt ion signal (in most of these spectra the most intense signal) indicates extensive dissociation of the Sn—S bonds, which must therefore be relatively weak.

Crystal structure of $[SnEt_2Cl_2(Hmimt)_2]$

Atomic coordinates for $[SnEt_2Cl_2(Hmimt)_2]$ are reported in Table 2, and bond lengths and angles in Table 3. The molecule is centrosymmetric, and in the crystal lattice the tin atom occupies a special position at a crystallographic inversion centre.

The tin atom is coordinated to two ethyl carbon atoms, two chlorine atoms and the sulfur atoms of two Hmimt ligands in an all-*trans* distorted octahedral arrangement (Fig. 1). The Sn—C and Sn—Cl bond lengths are in the ranges found for related systems in the Cambridge Crystallographic Data Base, 2.099–2.158 Å and 2.575–2.759 Å,

Table 2 Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $[SnEt_2Cl_2(Hmimt)_2]$

Atom	*x*	*y*	*z*	U_{eq}[a]
Sn	0	0	0	34(1)
S	697(1)	1353(1)	−2159(1)	49(1)
Cl	1520(1)	1577(1)	1795(1)	57(1)
C(2)	865(3)	3008(3)	−1718(3)	38(1)
N(1)	2054(3)	3667(3)	−1144(3)	44(1)
N(2)	−172(3)	3920(3)	−1944(3)	43(1)
C(1)	3462(4)	3073(5)	−759(5)	65(1)
C(4)	353(5)	5157(3)	−1509(5)	54(1)
C(5)	1745(5)	4989(3)	−1010(5)	54(1)
C(6)	1736(4)	−1340(4)	7(6)	79(2)
C(7)	3123(4)	−908(5)	−84(5)	77(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

respectively.[15] The Sn—S bond is the longest found in $[SnR_2X_2(Hmimt)]$ or $[SnR_2X_2(Hmimt)_2]$ compounds.[6,9] The deviation from octahedral symmetry is apparent in the slight skew of the 'equatorial' plane $SClS^{\#1}Cl^{\#1}Sn$ [Cl—Sn—S = 93.48(3) °] and its slight tilt with respect to the C—Sn—C axis [C(6)—Sn—S = 90.15(14) °].

As in its complexes with other SnR_2X_2 species Hmimt is sulfur-monodentate. The C(2)—S bond is longer and the C(2)—N(2) bond shorter than the corresponding average distances in the free ligand,[16] indicating that, as previously,[6,9] coordination reduces C—S bond order and increases C—N bond order.

The orientation of the two Hmimt ligands [C(6)$^{\#1}$—Sn—S—C(2) = 53.38(18) °; Sn—S—C(2)—N(1) = 92.7(3) °] allows the formation of intermolecular hydrogen bonds (Table 3), which create the polymeric lattice shown in Fig. 2. In this, $[SnEt_2Cl_2(Hmimt)_2]$ differs from $[SnPh_2Cl_2(Hmimt)_2]$, which has only an intramolecular hydrogen bond. The difference is due to the relative rotations of Hmimt about the Sn—S and C—S bonds, as in cationic diorganotin(IV) complexes of type $[SnR_2(Hmimt)_4]^{2+}$.[17]

Vibrational spectra

The spectral pattern of the coordinated ligand in the range 3200–600 cm^{-1} is similar to that found for similar complexes in which, as was confirmed in this work for $[SnEt_2Cl_2(Hmimt)_2]$, it is sulfur-monodentate.[6,17] For the ethyl derivatives, both ν(Sn—C) vibrations were identified in the IR and Raman spectra, but rigorous identification of the asymmetric vibration of the butyl derivatives was not possible. Identification of ν(Sn—S) was possible only for the 1:1 compounds, for which it was

Table 3 Bond lengths (Å) and angles (°) in $[SnEt_2Cl_2(Hmimt)_2]$. E.s.d.s in parentheses refer to the last significant digit

Sn—C(6)	2.140(3)	N(1)—C(5)	1.368(4)
Sn—Cl	2.6226(8)	N(1)—C(1)	1.461(5)
Sn—S	2.7532(9)	N(2)—C(4)	1.377(4)
S—C(2)	1.715(3)	C(4)—C(5)	1.345(6)
C(2)—N(2)	1.338(4)	C(6)—C(7)	1.421(5)
C(2)—N(1)	1.349(4)		
C(6)$^{\#1}$—Sn—C(6)	180.0	C(2)—S—Sn	107.2(1)
Cl$^{\#1}$—Sn—Cl	180.0	N(2)—C(2)—N(1)	106.3(3)
S$^{\#1}$—Sn—S	180.0	N(2)—C(2)—S	125.8(2)
C(6)—Sn—Cl	92.6(1)	N(1)—C(2)—S	127.8(2)
C(6)—Sn—Cl$^{\#1}$	87.4(1)	C(2)—N(1)—C(5)	109.5(3)
C(6)—Sn—S	90.2(1)	C(2)—N(1)—C(1)	125.4(3)
C(6)—Sn—S$^{\#1}$	89.9(1)	C(5)—N(1)—C(1)	125.1(3)
Cl—Sn—S	93.48(3)	C(2)—N(2)—C(4)	110.1(3)
Cl—Sn—S$^{\#1}$	86.52(3)	N(2)—C(4)—C(5)	106.5(3)
C(7)—C(6)—Sn	123.3(3)	C(4)—C(5)—N(1)	107.6(3)

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	D—H—A
N(2)—H(111)…Cl$^{\#2}$	0.88(4)	2.35(4)	3.227(3)	174(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $x - 1/2, -y + 1/2, z - 1/2$.

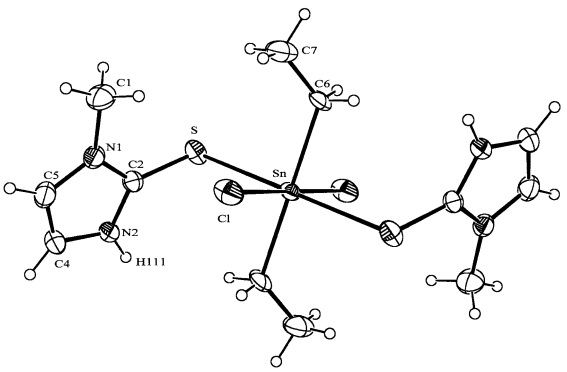

Figure 1 Molecular structure and atomic numbering scheme for $[SnEt_2Cl_2(Hmimt)_2]$. Atoms are represented as displacement ellipsoids drawn at the 30% probability level.

located close to its positions in the spectra of analogous methyl and phenyl derivatives.[6] For $[SnEt_2Cl_2(Hmimt)_2]$ ν(Sn—Cl) was found at a slightly higher wavenumber than in all-*trans* complexes with ligands with greater donor capacity.[18,19] In the 1:1 compound ν(Sn—Cl) is located at a higher wavenumber than in the 1:2 compound as a result of the lower coordination number. The complexity of the ligand spectra at low wavenumbers prevented rigorous assignment of the metal–halogen stretching bands for the bromide complexes.

Mössbauer spectra

The isomer shifts and line widths of the complexes are typical of a single tin site in each case. Like their methyl analogues,[6b] the 1:2 complexes have Δ values slightly less than 4.0 mm s^{-1} that are typical of the all-*trans* octahedral geometry confirmed by X-ray diffractometry for $[SnEt_2Cl_2(Hmimt)_2]$ in this work. The 1:1 complexes, all have quadrupole splittings of about 3.2 mm s^{-1} that are indicative of pentacoordination. Since $[SnMe_2Br_2(Hmimt)]$ also

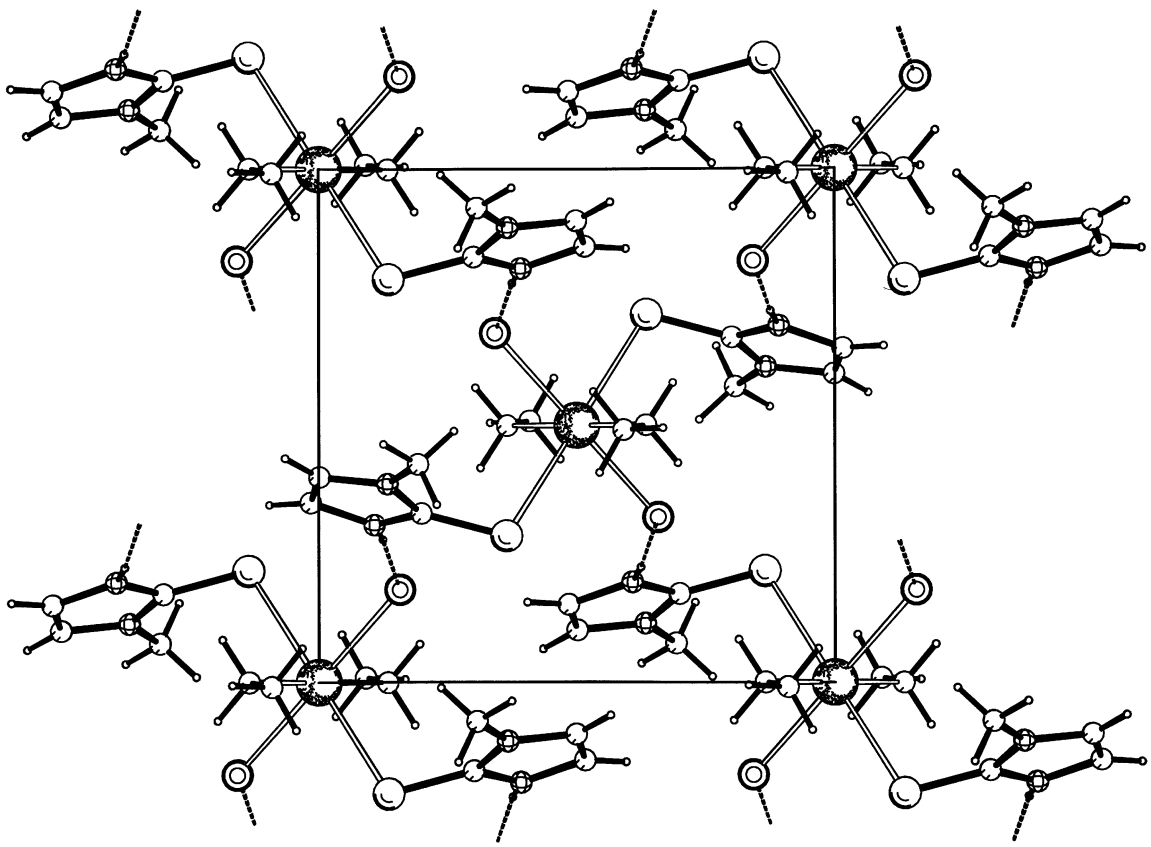

Figure 2 A view of the hydrogen-bonded polymeric structure of $[SnEt_2Cl_2(Hmimt)_2]$.

Table 4 ^{1}H, ^{13}C and ^{119}Sn NMR parameters for SnR_2 fragments (δ in ppm, J in Hz)

	^{1}H[a]					^{13}C					^{119}Sn	
Compound	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_2)$	$\delta(CH_2)$	^{2}J[b]	^{3}J[b]	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(CH_2)$	$\delta(CH_2)$	^{1}J[c]	^{2}J[c]	δ
$SnEt_2Cl_2$	1.43t	1.79q			50.3	135.9	9.1	18.3			430.9	39.8	120.0
$[SnEt_2Cl_2(Hmimt)]$	1.44t	1.86q			57.3	145.6	9.5	22.1			488.3	—	58.0
$[SnEt_2Cl_2(Hmimt)_2]$	1.43t	1.89q			60.7	151.4	9.8	24.3			529.8	44.0	16.9
$SnEt_2Br_2$	1.40t	1.85q			45.6	137.1	9.9	18.6			412.5	—	—
$[SnEt_2Br_2(Hmimt)]$	1.41t	1.90q			49.7	142.4	10.0	20.7			—	—	—
$[SnEt_2Br_2(Hmimt)_2]$	1.40t	1.94q			54.4	148.8	10.3	23.3			464.2	41.6	—
$SnBu_2Cl_2$	0.96t	1.42m	1.74–1.80m		—	—	13.4	26.2	26.9	26.9	421.2	43.0	126.2
$[SnBu_2Cl_2(Hmimt)]$	0.93t	1.43m	1.79m	1.89m	—	—	13.4	26.2	27.0	28.8	466.6	—	76.0
$SnBu_2Br_2$	0.96t	1.43m	1.79m	1.89m	—	—	13.4	26.0	26.9	27.6	391.8	—	—
$[SnBu_2Br_2(Hmimt)]$	0.94t	1.41m	1.77m	1.93m	—	—	13.4	26.0	27.6	28.4	—	—	—

[a] t = triplet; q = quartet; m = multiplet.
[b] $J(^{1}H–^{119}Sn)$.
[c] $J(^{13}C–^{119}Sn)$.

has a Δ value strongly suggestive of trigonal bipyramidal coordination (3.13 mm s^{-1}),[6b] the only $[SnR_2X_2(Hmimt)]$ compound in which the tin atom achieves hexacoordination (by formation of an Sn…X—Sn bridge with a neighbouring molecule) is $[SnMe_2Cl_2(Hmimt)]$,[6b] for which X-ray diffractometry shows a severely distorted octahedral coordination polyhedron with a C—Sn—C angle of 144.2(3)° in keeping with the quadrupole splitting of 3.63 mm s^{-1}. Thus hexacoordination in the $[SnR_2X_2(Hmimt)]$ series (R = Me, Et, Bu) appears to require both a good bridging halogen (Cl is better than Br in this respect) and an R group that is small enough for C—Sn—C distortion and the approach of a neighbouring molecule to be sterically feasible, Me being apparently the only R group satisfying this criterion.

Characteristics in solution

The molar conductivities of 10^{-3}M solutions of the complexes in acetonitrile show them all to be non-ionogenic in this solvent.[20]

^1H, ^{13}C and ^{119}Sn chemical shifts and coupling constants for the SnR_2 fragments of the acceptors and complexes in $CDCl_3$ are reported in Table 4. Chemical shifts for the Hmimt moieties have been omitted because they differ very little from those of the free ligand. This absence of significant modification of the Hmimt spectrum, together with the similarity between the SnR_2 fragment signals and those of the free acceptors, suggests that the complexes significantly dissociate in solution, as do the Hmimt complexes of $SnMe_2X_2$ and $SnPh_2X_2$[6] and other compounds with monodentate ligands.[18,21] This is corroborated by the ^{119}Sn chemical shifts[6b,6c] and by the observed coupling constants [for the butyl derivatives the complexity of the 0–2 ppm zone of the ^1H spectrum and the 10–30 ppm zone of the ^{13}C spectrum prevented measurement of $^2J(^1H–Sn)$ and $^1J(^{13}C–Sn)$].

Antibacterial activity

Table 5 shows the antibacterial activities of Hmimt, the diethyl- and dibutyltin(IV) dihalides, and their complexes. In our hands, Hmimt was only active against *B. subtilis*, despite a previous report of slight activity against *E. coli*.[8] All the assayed diorganotin(IV) dihalides and complexes showed activity against the Gram-negative bacterium *E. coli* and the Gram-positive bacteria *S. aureus* and *B. subtilis*, with MIC values that were generally lower for the butyl than the corresponding ethyl derivatives. Bearing in mind the slightly different experimental conditions, the MICs of the diorganotin dihalides were in accord with those previously reported.[22,23] Only $SnEt_2Cl_2$, $[SnEt_2Cl_2(Hmimt)]$ and $SnBu_2Br_2$ showed a slight activity against the Gram-negative *P. aeruginosa*, with MIC values similar to those found by Nath and Goyal[24] for some diorganotin complexes of Schiff bases.

Complexation with Hmimt marginally increased the activity of $SnEt_2Cl_2$ against *E. coli* and *S. aureus*, but reduced or had no effect on the activity of the other diorganotin dihalides. In those cases in which activity was unaltered, this lack of effect may be attributed to the dissociation discussed above and the low or zero activity of Hmimt. The MIC values found in this case show a comparable or

Table 5 Antibacterial activities of Hmimt, diorganotin(IV) dihalides and their complexes

	MIC (μg ml^{-1})			
Compound	*E. coli*	*P. aeruginosa*	*S. aureus*	*B. subtilis*
Hmimt	—	—	—	6.25
$SnEt_2Cl_2$	25	50	25	6.25
$[SnEt_2Cl_2(Hmimt)]$	12.5	50	25	6.25
$[SnEt_2Cl_2(Hmimt)_2]$	12.5	—	12.5	6.25
$SnEt_2Br_2$	12.5	—	12.5	6.25
$[SnEt_2Br_2(Hmimt)]$	25	—	25	6.25
$[SnEt_2Br_2(Hmimt)_2]$	25	—	25	6.25
$SnBu_2Cl_2$	12.5	—	6.25	3.12
$[SnBu_2Cl_2(Hmimt)]$	12.5	—	6.25	3.12
$SnBu_2Br_2$	6.25	50	6.25	6.25
$[SnBu_2Br_2(Hmimt)]$	12.5	—	6.25	6.25

greater antibacterial activity against *E. coli*, *S. aureus* and *B. subtilis* than those found previously for the complexes of these acceptors with ligands like hydrazones[22,23,25] or thio Schiff bases.[24]

In a previous paper[26] we reported that some triphenyltin(IV) sulfanylpropenoates were more active against Gram-positive than against Gram-negative bacteria. The compounds listed in Table 5 were almost all more active against the Gram-positive *B. subtilis* than against the Gram-negative *E. coli*, and most of the butyl compounds (but not the ethyl derivatives) were also more active against *S. aureus* than *E. coli*, but the differences are generally less marked than with the triphenyltin derivatives.

Acknowledgements We thank the Xunta de Galicia, Spain, for financial support.

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