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Diorganotin Dihalide Complexes of *N*-bidentate Ligands: Crystal Structures of Diethyldibromo- and Dibutyldichloro[bis(1-methyl-2-imidazolylthio)methane]tin(IV)

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The compounds $[SnR_2X_2(bmimt)]$ (R = Me, Et, Bu; X = Cl, Br; bmimt = bis(1-methyl-2-imidazolylthio)methane) have been prepared and characterized by conductivity measurements and by IR, Raman, mass, Mössbauer and ^{1}H NMR spectroscopy. The structures of the diethyldibromo- and dibutyldichlorotin(IV) derivatives were determined by X-ray crystallography. The crystals consist of two slightly different types of discrete $[SnR_2X_2(bmimt)]$ unit with the metal atom octahedrally coordinated to the two halogen atoms, two alkyl carbons and the two nonmethylated nitrogen atoms of the ligand. This coordination mode, which the spectroscopic data suggest is also present in all the other complexes studied, results in the formation of an eight-membered $CS_2C_2N_2Sn$ ring. The Sn– N distances in $[SnEt_2Br_2(bmimt)]$ (2.53 and 2.42 Å) and $[SnBu_2Cl_2(bmimt)]$ (2.52 and 2.47 Å), suggest that these compounds may have antitumour activity. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: tin; dialkyltin dihalide complexes; bis(1-methyl-2-imidazolylthio)methane complexes; crystal structure; vibrational spectroscopy; NMR spectroscopy

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INTRODUCTION

Compounds of the type $[SnR_2X_2(L\text{-}L)]$, where L–L is a bidentate *N,N′*-donor ligand, have been extensively studied and screened *in vivo* and *in vitro* for antitumour activity, usually against P388 lymphocytic leukaemia.[1] The mechanism of this activity is still under discussion. However, studies of structure–activity relationships show that the Sn–N distance is important, the average Sn–N bond length being $\geq$2.39 Å among active complexes and $<$2.39 Å among inactive complexes. It has been suggested[1] that the more stable complexes have lower activities, which in turn implies that predissociation of the bidentate ligand may be an important step in the mode of action of these complexes.

In previous work we synthesized $[SnR_2X_2(L\text{-}L)]$ compounds whose activity *in vitro* was determined[2,3] or for which the Sn–N distance suggested low activity.[4,5] In these compounds, as in the majority of those whose structures have been studied,[6] the *N,N′*-coordinate ligand originated a five-membered SnN_2C_2 ring, but recently a six-membered SnN_4C ring with Sn–N bond distances $>$ 2.39 Å has been reported in the adduct of dichlorodimethyltin(IV) with bis(4-methylpyrazol-l-yl)methane.[6] This, and our general interest in the study of compounds with ligands which are potentially able to form large rings with long Sn–N bonds, led us to prepare the ligand bis(1-methyl-2-imidazolylthio)methane, bmimt (**I**), and its complexes with the dialkyltin dihalides SnR_2X_2 (R = Me, Et and Bu; X = Cl, Br). This paper describes their synthesis, their conductimetric and

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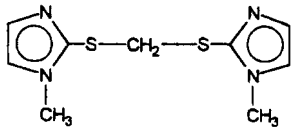
spectroscopic properties in the solid state and/or in solution, and the crystal structures of $[SnEt_2Br_2$(bmimt)] and $[SnBu_2Cl_2$(bmimt)], which contain eight-membered $CS_2C_2N_2Sn$ rings in which the Sn–N distances suggest possible antitumour activity.



bmimt (I)

EXPERIMENTAL DETAILS

Materials and measurements

Diorganotin dihalides (Alfa and Aldrich) and 1-methyl-2(3*H*)-imidazolinethione (Aldrich) were used as supplied. Solvents were dried by standard methods.

Elemental analysis was performed with a Carlo–Erba 1108 apparatus. Melting points were measured with a Büchi apparatus. IR spectra (in Nujol mulls or KBr discs) and Raman spectra (polycrystalline samples) were recorded on a Bruker IFS66V FT-IR spectrometer equipped with a Bruker FRA 106 accessory. Mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a DS90 or MACH3 system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C); all ions were identified by DS90 or MACH3 software. Mössbauer spectra were recorded at 80 K using 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 spectra. Conductivity measurements were made using a WTW-LF3 conductivity meter. ^1H and ^{13}C NMR spectra in $CDCl_3$ were run on a Bruker AMX 300 apparatus at 300.14 and 75.48 MHz respectively; chemical shifts, in ppm, are referred to TMS via the solvent peak.

Synthesis

The bmimt ligand

1-Methyl-2(3*H*)-imidazolinethione (Hmimt) (2.984 g, 26.1 mmol) was added to a solution of NaOH (1.045 g, 26.1 mmol) in 40 ml of absolute ethanol. After one day's stirring the solvent was evaporated off and the sodium salt so obtained was suspended in CH_2Cl_2, and this mixture was stirred for six days and then refluxed for 12 h. The solid was filtered off and the filtrate was concentrated *in vacuo*, affording an orange oil which was purified on a silica gel column using ethyl acetate/methanol as eluent.

General procedure for $[SnR_2X_2$(bmimt)]

All the compounds were prepared by slow addition of a solution of the appropriate diorganotin(IV) derivative in dry CH_2Cl_2 (*ca* 20 ml) to a solution of bmimt in *ca* 20 ml of the same solvent. The mixture was stirred for one day, and after refluxing for 4 h the solvent was partially evaporated and the solid so obtained was filtered off and dried *in vacuo*.

$[SnMe_2Cl_2$(bmimt)]

From 0.543 g $SnMe_2Cl_2$ (2.5 mmol) and 0.594 g bmimt (2.5 mmol). Analysis: Found: C 28.3, H 3.8, N 11.5, S 13.6; Calcd for $C_{11}H_{18}Cl_2N_4S_2Sn$: C 28.7, H 3.9, N 12.2, S 13.9%. M.p. 187 °C. Λ_M (CH_3CN) = 21.7 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity, based on isotope ^{120}Sn): 114 (Hmimt, 24.4); 120 (Sn, 4.6); 127 (Hmimt − H + CH_2, 100); 155 (SnCl, 17.6); 185 ($SnMe_2Cl$, 9.0); 194 ($C_8H_{10}N_4S$, 47.0); 205 ($SnMeCl_2$, 35.2); 220 ($SnMe_2Cl_2$, 1.4).

$[SnMe_2Br_2$(bmimt)]

From 0.424 g $SnMe_2Br_2$ (1.4 mmol) and 0.331 g bmimt (1.4 mmol). Analysis: Found: C 24.0, H 3.3, N 9.9, S 11.2; Calcd for $C_{11}H_{18}Br_2N_4S_2Sn$: C 24.1, H 3.3, N 10.2, S 11.7%. M.p. 175 °C. Λ_M (CH_3CN) = 26.7 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 114 (Hmimt, 27.9); 120 (Sn, 18.5); 127 (Hmimt − H + CH_2, 96.0); 194 ($C_8H_{10}N_4S$, 38.3); 199 (SnBr, 61.3); 229 ($SnMe_2Br$, 22.3); 278 ($SnBr_2$, 4.3); 293 ($SnMeBr_2$, 100.0); 308 ($SnMe_2Br_2$, 9.9).

$[SnEt_2Cl_2$(bmimt)]

From 0.075 g $SnEt_2Cl_2$ (0.3 mmol) and 0.073 g bmimt (0.3 mmol). Analysis: Found: C 32.3, H 4.6, N 11.3, S 13.4; Calcd for $C_{13}H_{22}Cl_2N_4S_2Sn$: C 32.0, H 4.5, N 11.5, S 13.1%. M.p. 162 °C. Λ_M (CH_3CN) = 12.5 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 114 (Hmimt, 25.3); 120 (Sn, 8.1); 127 (Hmimt − H + CH_2, 100.0); 155 (SnCl, 53.0); 184 (SnEtCl, 8.4); 194 ($C_8H_{10}N_4S$, 47.8); 219 ($SnEtCl_2$, 43.5); 248 ($SnEt_2Cl_2$ 5.4).

Table 1 Crystal data and structure refinement for [$SnEt_2Br_2$(bmimt)] and [$SnBu_2Cl_2$(bmimt)]

Empirical formula	$C_{13}H_{22}Br_2N_4S_2Sn$	$C_{17}H_{30}Cl_2N_4S_2Sn$
Formula weight	576.98	544.16
Temperature	293(2) K	293(2) K
Wavelength	1.54184 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2/n$
Unit cell dimensions	a = 16.406(2) Å	a = 15.560(13) Å
	b = 13.934(2) Å	b = 9.604(5) Å
	c = 18.790(2) Å	c = 16.055(13) Å
	β = 110.94(1)°	β = 103.06(2)°
Volume	4011.9(9) Å^3	2337(3) Å^3
Z, density (calcd)	8, 1.910 Mg m^{-3}	4, 1.546 Mg m^{-3}
Absorption coefficient	16.753 mm^{-1}	1.510 mm^{-1}
F(000)	2240	1104
Crystal size	0.35 mm × 0.15 mm × 0.10 mm	0.25 mm × 0.25 mm × 0.15 mm
θ range for data collection	2.88 – 74.63°	3.29 – 28.95°
Index ranges	$-19 \le h \le 20$, $0 \le k \le 17$, $-23 \le l \le 0$	$0 \le h \le 21$, $0 \le k \le 6$, $-21 \le l \le 21$
Reflections collected/unique	8477/8214 [R_{int} = 0.0187]	4111/3984 [R_{int} = 0.0674]
Absorption correction	Empirical	Empirical
Max. and min. transmission	1.000 and 0.075	0.8052 and 0.7040
Refinement method		Full-matrix and least-squares on F^2
Data/restraints/parameters	8214/0/406	3984/0/265
Goodness-of-fit on F^2	1.088	1.023
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0661, wR_2 = 0.1876	R_1 = 0.0493, wR_2 = 0.1094
R indices (all data)	R_1 = 0.0997, wR_2 = 0.2108	R_1 = 0.0974, wR_2 = 0.1267
Largest diff. peak and hole	1.221 and −1.505 e Å^{-3}	0.571 and −0.923 e Å^{-3}

[$SnEt_2Br_2$(bmimt)]
From 0.562 g $SnEt_2Br_2$ (1.7 mmol) and 0.401 g bmimt (1.7 mmol). Analysis: Found: C 26.9, H 3.9, N 9.4, S 10.6; Calcd for $C_{13}H_{22}Br_2N_4S_2Sn$: C 27.1, H 3.8, N 9.7, S 11.1%. M.p. 145 °C. Λ_M (CH_3CN) = 24.3 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 114 (Hmimt, 13.0); 120 (Sn, 30.0); 127 (Hmimt − H + CH_2, 51.2); 194 ($C_8H_{10}N_4S$, 18.0); 199 (SnBr, 100.0); 228 (SnEtBr, 7.6); 278 ($SnBr_2$, 9.9); 307 ($SnEtBr_2$, 66.1); 336 ($SnEt_2Br_2$, 5.3).

[$SnBu_2Cl_2$(bmimt)]
From 0.676 g $SnBu_2Cl_2$ (2.2 mmol) and 0.535 g bmimt (2.2 mmol). Analysis: Found: C 37.5, H 5.5, N 10.0, S 11.7; Calcd for $C_{17}H_{30}Cl_2N_4S_2Sn$: C 37.5, H 5.6, N 10.3, S 11.8%. M.p. 148 °C. Λ_M (CH_3CN) = 25.9 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 57 (Bu, 100.0); 114 (Hmimt, 18.2); 127 (Hmimt − H + CH_2, 73.2); 155 (SnCl, 15.5); 194 ($C_8H_{10}N_4S$, 36.9); 212 (SnBuCl, 8.7); 247 ($SnBuCl_2$, 10.3); 269 ($SnBu_2Cl$, 2.2).

[$SnBu_2Br_2$(bmimt)]
From 0.425 g $SnBu_2Br_2$ (1.1 mmol) and 0.260 g bmimt (1.1 mmol). Analysis: Found: C 32.0, H 5.0, N 8.4, S 9.3; Calcd for $C_{17}H_{30}Br_2N_4S_2Sn$: C 32.2, H 4.8, N 8.8, S 10.1% M.p. 125 °C. Λ_M (CH_3CN) = 29.6 S cm^2 mol^{-1}. The mass spectrum showed peaks at *m/z* (ion, intensity): 57 (Bu, 100.0); 114 (Hmimt, 3.2); 120 (Sn, 10.9); 127 (Hmimt − H + CH_2, 12.0); 177 (SnBu, 4.9); 194 ($C_8H_{10}N_4S$, 3.9); 199 (SnBr, 49.6); 278 ($SnBr_2$, 4.2); 313 ($SnBu_2Br$, 3.7); 335 ($SnBuBr_2$, 44.0); 392 ($SnBu_2Br_2$, 1.6).

Crystal structure determination

X-ray data collection and reduction

Crystals suitable for X-ray diffraction studies were obtained by slow concentration of solutions of [$SnEt_2Br_2$(bmimt)] and [$SnBu_2Cl_2$(bmimt)] in chloroform. Cell constants and an orientation matrix for data collection were obtained with an Enraf–Nonius CAD-4 automatic diffractometer by least-squares refinement of the diffraction data from 25 reflections in the range $22.8° < \theta < 42.2°$ for the ethyl derivative and $8.5° < \theta < 12.0°$ for the butyl derivative.[7] Data were collected by ω-scan at 293(2) K using CuK_α radiation (λ = 1.54184 Å) for the ethyl derivative and MoK_α radiation (λ = 0.71073 Å) for the butyl derivative, and were corrected for Lorentz and polarization effects.[8] An empirical absorption correction was also made.[9] A summary of the crystal data, experimental details and refinement results are listed in Table 1.

Structure solution and refinement

Both structures were solved by direct methods,[10] which revealed the positions of all the non-hydrogen atoms, and were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for non-hydrogen atoms.[11] For the ethyl derivative, the hydrogen atoms of the imidazole ring were located in calculated positions (C–H = 0.93 – 0.97 Å) and were refined using a rigid model; for the butyl derivative, the hydrogen atoms of the imidazole ring were located from difference maps and refined isotropically, and other hydrogen atoms were located and refined as for the ethyl derivative. For this latter compound relatively large positive peaks were found in the final difference Fourier map, but these were all error peaks located near the Sn and Br atoms. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography*[12] and graphics were produced using the programs ZORTEP[13] and PLATON.[14]

RESULTS AND DISCUSSION

Crystal structure of $[SnEt_2Br_2(bmimt)]$

Figure 1 shows a ZORTEP view of the two slightly different types of $[SnEt_2Br_2(bmimt)]$ molecule present in the asymmetric unit of the crystal [molecule **1** contains Sn(1) and molecule **2** Sn(2)]. Table 2 lists positional parameters and Table 3 selected distances and angles.

In both molecules the tin atom has slightly distorted octahedral coordination to two *trans* ethyl C atoms, two *cis* Br atoms and two *cis* N atoms (the non-methylated N atoms of the bidentate bmimt ligand). The Sn–C and Sn–N bond lengths are longer in **2** than in **1**, but while one of the Sn–Br distances is longer in **1** than in **2**, the other is longer in **2** than in **1**. In both molecules the longer Sn–N bond is *trans* to the shorter Sn–Br bond. A recent review of similar $SnR_2X_2N_2$ structures[6] found reports of Sn–C distances ranging from 2.047(32) to 2.22(1) Å, Sn–N from 2.270(26) to 2.608(5) Å and Sn–Br from 2.643(3) to 2.767(2) Å (although

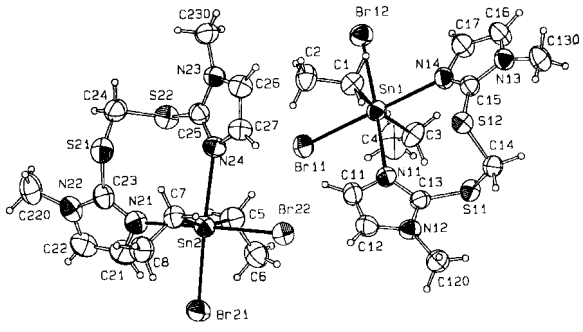


Figure 1 Perspective view of $[SnEt_2Br_2(bmimt)]$ showing the atom numbering scheme.

Table 2 Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^{-3}$) for $[SnEt_2Br_2(bmimt)]$[a]

	x	*y*	*z*	*U*(eq)
Sn(1)	8044(1)	7873(1)	116(1)	67(1)
Sn(2)	3043(1)	7457(1)	−1389(1)	77(1)
Br(11)	6964(1)	6936(1)	−1107(1)	94(1)
Br(12)	8908(1)	8759(1)	−690(1)	88(1)
Br(21)	2286(1)	5855(1)	−1178(1)	106(1)
Br(22)	3715(1)	7748(1)	170(1)	94(1)
S(11)	8433(2)	6697(2)	2167(1)	78(1)
S(12)	8087(2)	8829(2)	2215(2)	77(1)
S(21)	2131(2)	8961(2)	−3371(2)	96(1)
S(22)	4098(2)	8733(2)	−2868(2)	95(1)
N(11)	7201(5)	7118(6)	786(5)	76(2)
N(12)	6670(6)	6595(6)	1628(5)	77(2)
N(13)	9700(5)	9445(6)	2368(4)	75(2)
N(14)	9018(5)	8754(6)	1263(5)	76(2)
N(21)	2440(6)	7158(7)	−2755(6)	87(2)
N(22)	1838(6)	7178(9)	−4015(6)	95(3)
N(23)	4461(5)	10210(6)	−1835(5)	77(2)
N(24)	3824(6)	8971(6)	−1526(5)	79(2)
C(11)	6303(7)	7116(9)	469(7)	90(3)
C(12)	5974(7)	6800(9)	978(7)	89(3)
C(13)	7394(7)	6788(7)	1495(5)	71(2)
C(14)	8418(7)	7734(7)	2744(5)	77(3)
C(15)	8954(6)	9012(7)	1932(5)	70(2)
C(16)	10251(7)	9477(9)	1972(6)	91(3)
C(17)	9827(8)	9051(9)	1294(7)	90(3)
C(21)	2329(9)	6251(10)	−3021(9)	109(4)
C(22)	1949(10)	6258(11)	−3793(9)	107(4)
C(23)	2134(8)	7705(9)	−3365(7)	89(3)
C(24)	3118(9)	9201(9)	−3567(7)	99(4)
C(25)	4111(7)	9331(8)	−2048(6)	82(3)
C(26)	4387(8)	10425(8)	−1159(7)	87(3)
C(27)	3994(7)	9659(8)	−976(7)	84(3)
C(120)	6607(8)	6218(10)	2329(6)	94(3)
C(130)	9906(8)	9804(9)	3149(6)	96(3)
C(220)	1436(10)	7539(13)	−4779(8)	123(5)
C(230)	4868(8)	10816(10)	−2233(8)	99(4)
C(1)	7238(7)	9120(7)	0(6)	76(2)
C(2)	6548(8)	9320(10)	−749(7)	101(4)
C(3)	8991(8)	6737(9)	462(6)	88(3)
C(4)	9124(12)	6119(13)	−94(10)	153(8)
C(5)	4246(8)	6795(9)	−1367(8)	94(3)
C(6)	4501(9)	5893(10)	−949(8)	107(4)
C(7)	1959(7)	8431(8)	−1527(7)	83(3)
C(8)	1064(8)	8003(10)	−1852(9)	109(4)

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

Table 3 Selected bond lengths (Å) and angles (°) for $[SnEt_2Br_2(bmimt)]$

Sn(1)–C(1)	2.147(9)	Sn(2)-C(5)	2.165(11)
Sn(1)–C(3)	2.149(10)	Sn(2)-C(7)	2.177(10)
Sn(1)–N(11)	2.417(8)	Sn(2)-N(21)	2.435(10)
Sn(1)–N(14)	2.498(8)	Sn(2)-N(24)	2.529(9)
Sn(1)–Br(11)	2.686(1)	Sn(2)-Br(21)	2.652(2)
Sn(1)–Br(12)	2.713(1)	Sn(2)-Br(22)	2.765(2)
C(1)-Sn(1)-C(3)	168.3(4)	C(5)-Sn(2)-C(7)	165.4(5)
C(1)-Sn(1)-N(11)	87.7(4)	C(5)-Sn(2)-N(21)	88.4(4)
C(3)-Sn(1)-N(11)	90.5(4)	C(7)-Sn(2)-N(21)	88.5(4)
C(1)-Sn(1)-N(14)	82.6(4)	C(5)-Sn(2)-N(24)	82.3(4)
C(3)-Sn(1)-N(14)	86.0(4)	C(7)-Sn(2)-N(24)	83.7(4)
N(11)-Sn(1)-N(14)	94.2(3)	N(21)-Sn(2)-N(24)	93.7(3)
C(1)-Sn(1)-Br(11)	96.5(3)	C(5)-Sn(2)-Br(21)	96.4(3)
C(3)-Sn(1)-Br(11)	94.9(3)	C(7)-Sn(2)-Br(21)	97.8(3)
N(11)-Sn(1)-Br(11)	84.8(2)	N(21)-Sn(2)-Br(21)	88.7(2)
N(14)-Sn(1)-Br(11)	178.6(2)	N(24)-Sn(2)-Br(21)	177.1(2)
C(1)-Sn(1)-Br(12)	90.0(3)	C(5)-Sn(2)-Br(22)	91.5(4)
C(3)-Sn(1)-Br(12)	92.2(3)	C(7)-Sn(2)-Br(22)	92.0(3)
N(11)-Sn(1)-Br(12)	176.9(2)	N(21)-Sn(2)-Br(22)	178.5(2)
N(14)-Sn(1)-Br(12)	87.5(2)	N(24)-Sn(2)-Br(22)	87.8(2)
Br(11)-Sn(1)-Br(12)	93.45(4)	Br(21)-Sn(2)-Br(22)	89.75(5)

no Sn–Br distance concerned a diethyldibromotin(IV) derivative of similar structure to $[SnEt_2Br_2(bmimt)]$). The Sn–C, Sn–N and Sn–Br distances in $[SnEt_2Br_2(bmimt)]$ fall within the range found hitherto for $SnR_2Br_2N_2$ complexes.

Molecules **1** and **2** differ slightly as regards the angles between coordinate bonds. In particular, Br(11)-Sn(1)-Br(12) = 93.45(4)° as against Br(21)-Sn(2)-Br(22) = 89.75(5)°, and C(1)-Sn(1)-C(3) = 168.3(4)° whereas C(5)-Sn(2)-C(7) = 165.4(5)°, although the N-Sn-N angles in the two molecules have similar values. Note that in both molecules the non-equivalence of the Sn–N bonds affects the orientation of the C-Sn-C distortion; for example, C(1)-Sn(1)-N(11) = 87.7(4)° whereas C(1)-Sn(1)-N(14) = 82.6(4)°.

There are also slight differences between the two molecules as regards the coordination mode of bmimt. The imidazole rings are essentially planar in both [for example, $\chi^2 = 0.002$ for N(11)C(11)C(12) N(12)C(13)], and the methyl C and S atoms are close to the least-squares imidazole plane [C(120) and S(11) lie respectively 0.012 and 0.082 Å from it] but the Sn atom is somewhat farther away [0.350 Å in the most extreme case,that of Sn(1)]. The angle between the imidazole ring and the least-squares plane through its coordinated N, the Br *trans* to it and the two coordinated ethyl carbon atoms ranges from 49.8° for [N(11)C(11)C(12) N(12)C(13)] / [C(1)Br(12)C(3) N(11)] to 56.2° for [N(21)C(21)C(22)N(22)C(23)] / [C(5)Br(22)C(7) N(21)]. The remaining ligand parameters are similar in the two molecules.

Crystal structure of $[SnBu_2Cl_2(bmimt)]$

As in the ethyl derivative, there are two different types of molecule in the crystal of $[SnBu_2Cl_2(bmimt)]$. Figure 2 shows a view of molecule **1** [containing Sn(1)] and Fig. 3 a view of molecule **2** [containing Sn(2)]; the asymmetric unit comprises one half of each molecule. Table 4 lists positional parameters and Table 5 selected distances and angles.

In both molecules the tin atom has slightly distorted octahedral coordination to two *trans* butyl C atoms, two *cis* Cl and two *cis* N atoms (the non-methylated N atoms of the bidentate bmimt ligand).

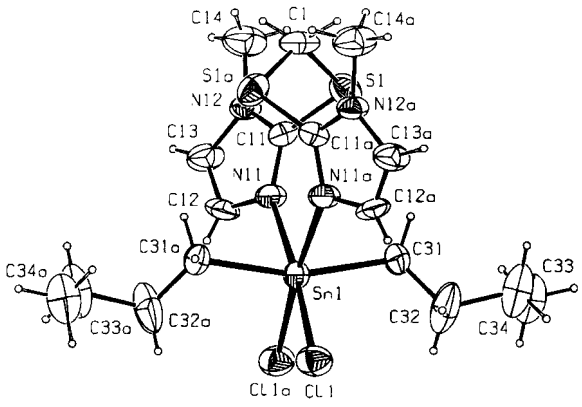


Figure 2 View of molecule **1** of $[SnBu_2Cl_2(bmimt)]$ showing the atom numbering scheme.

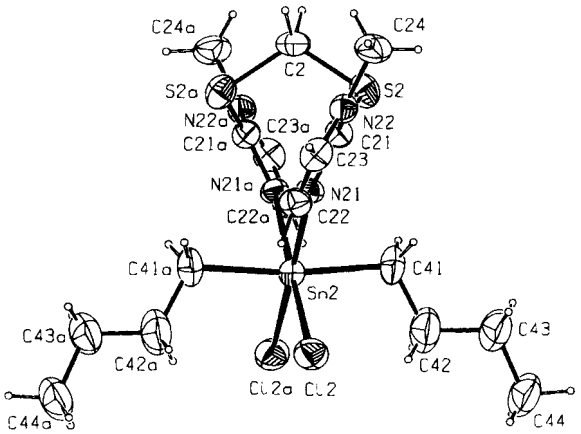


Figure 3 View of molecule **2** of $[SnBu_2Cl_2(bmimt)]$ showing the atom numbering scheme.

The Sn–C bond lengths are practically equal in the two $SnC_2Cl_2N_2$ kernels, but Sn–N is shorter and Sn–Cl longer in **2** than in **1**. For similar $SnR_2X_2N_2$ structures Sn–C ranges from 2.047(32) to 2.22(1) Å, Sn–N from 2.270(26) to 2.608(5) Å and Sn–Cl from 2.440(1) to 2.609(10) Å;[6] in particular, for the three dibutyl derivatives previously studied Sn–C ranges from 2.09(1) to 2.22(1) Å, Sn–N from 2.35(2) to 2.43(1) Å and Sn–Cl from 2.451(2) to 2.561(1) Å. Whereas the Sn–C and Sn–Cl distances in $[SnBu_2Cl_2(bmimt)]$ are within the ranges found in the dibutyl complexes studied previously, the Sn–N bonds are longer, although they fall within the general range found for $SnR_2Cl_2N_2$ complexes. In both molecules, as in the ethyl derivative, the Sn–N bond lengths are >2.39 Å, which suggests that these compounds may have antitumour activity.[1]

Table 4 Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($Å^2 \times 10^{-3}$) for $[SnBu_2Cl_2(bmimt)]$[a]

	x	*y*	*z*	*U*(eq)
Sn(1)	7500	8464(1)	7500	32(1)
Cl(1)	6472(1)	10271(2)	6703(1)	48(1)
S(1)	7330(1)	4520(2)	6518(1)	46(1)
N(11)	8653(3)	6786(8)	8294(3)	36(2)
N(12)	5541(3)	4901(8)	6290(3)	36(2)
C(1)	7500	3523(13)	7500	47(3)
C(11)	6364(4)	5461(10)	6527(4)	34(2)
C(12)	9548(6)	7063(12)	8435(6)	47(3)
C(13)	4967(5)	5954(10)	6337(5)	49(2)
C(14)	5296(5)	3487(10)	6046(6)	63(3)
C(31)	6871(4)	8132(8)	8536(4)	40(2)
C(32)	6193(6)	9156(11)	8636(5)	76(3)
C(33)	5726(5)	8796(12)	9372(5)	76(3)
C(34)	6292(5)	8961(11)	10196(5)	75(3)
Sn(2)	2500	5712(1)	7500	34(1)
Cl(2)	2097(1)	3955(2)	8540(1)	51(1)
S(2)	3505(1)	9632(2)	7615(1)	45(1)
N(21)	2126(3)	7491(7)	8477(3)	33(2)
N(22)	3418(3)	9250(7)	5910(3)	38(2)
C(2)	2500	10651(13)	7500	42(3)
C(21)	3261(4)	8720(9)	6654(4)	34(2)
C(22)	2227(5)	7231(11)	9332(4)	41(2)
C(23)	3108(4)	8271(9)	5281(4)	43(2)
C(24)	3852(5)	10532(9)	5792(5)	52(2)
C(41)	1158(4)	5863(9)	6792(5)	51(2)
C(42)	723(5)	4454(11)	6541(6)	82(3)
C(43)	−239(5)	4437(11)	6276(7)	79(3)
C(44)	−628(5)	3039(11)	6068(7)	92(4)

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

The environments of Sn in molecules **1** and **2** differ not only in the bond lengths (Table 5) but also in the angles. $Cl(1)^a$-Sn(1)-Cl(1) = 92.35(11)° whereas $Cl(2)^b$-Sn(2)-Cl(2) = 97.14(11)°, and $N(11)^a$-Sn(1)-N(11) = 100.9(3) whereas $N(21)^b$-Sn(2)-N(21) = 92.7(3)°. The greater N-Sn-N angle

Table 5 Selected bond lengths (Å) and angles (°) for $[SnBu_2Cl_2(bmimt)]$

Sn(1)–C(31)	2.136(6)	Sn(2)-C(41)	2.144(6)
Sn(1)–Cl(1)	2.507(2)	Sn(2)-Cl(2)	2.550(2)
Sn(1)–N(11)	2.531(7)	Sn(2)-N(21)	2.476(6)
$C(31)^a$-Sn(1)-C(31)	162.9(4)	$C(41)^b$-Sn(2)-C(41)	172.3(5)
$C(31)^a$-Sn(1)-Cl(1)	93.3(2)	$C(41)^b$-Sn(2)-Cl(2)	93.0(2)
C(31)-Sn(1)-Cl(1)	98.6(2)	C(41)-Sn(2)-Cl(2)	92.2(2)
C(31)-Sn(1)-N(11)	84.8(2)	C(41)-Sn(2)-N(21)	87.1(2)
$C(31)$-Sn(1)-$N(11)^a$	84.3(2)	C(41)-Sn(2)-$N(21)^b$	87.6(2)
$Cl(1)^a$-Sn(1)-Cl(1)	92.35(11)	$Cl(2)^b$-Sn(2)-Cl(2)	97.14(11)
Cl(1)-Sn(1)-$N(11)^a$	83.45(17)	Cl(2)-Sn(2)-$N(21)^b$	177.80(15)
Cl(1)-Sn(1)-N(11)	174.77(16)	Cl(2)-Sn(2)-N(21)	85.05(16)
$N(11)^a$-Sn(1)-N(11)	100.9(3)	$N(21)^b$-Sn(2)-N(21)	92.7(3)

Symmetry transformations used to generate equivalent atoms: a $-x+3/2, y, -z+3/2$
b $-x+1/2, y, -z+3/2$

in **1** correlates with a greater Sn–N distance. The angular distortion from regular octahedral geometry is, except for the Cl-Sn-Cl angle, greater in molecule **1** than in molecule **2:** for example, C(31)[a]-Sn(1)-C(31) = 162.9(4)°, whereas C(41)[b]-Sn(2)-C(41) = 172.3(5)°.

As in the ethyl derivative, the coordination mode of bmimt is similar in both molecules, but there are nevertheless differences that are worth mentioning. The imidazole rings are planar as in the ethyl derivative (for example, $\chi^2 = 0.1819$ for N(11)C(11)C(12)N(12)C(13)), but the methyl C, the S and the Sn atoms lie farther from the imidazole plane than in [$SnEt_2Br_2$(bmimt)] [0.8341,0.0911 and 1.2292 Å for C(14),S(1) and Sn respectively]. The orientations of the imidazole rings with respect to the least-squares CXCN planes are, as in the ethyl derivative, different in **1** and **2:** for example, the angle between the N(11)C(11)C(12)N(12)C(13) and C(31)Cl(1)C(31)[a]N(11) planes is 73.68°, whereas the corresponding angle in **2** is 68.79°. In both [$SnBu_2Cl_2$(bmimt)] molecules these angles are wider than in the ethyl derivative. The smaller bite of the ligand in *2* (92.7° as against 100.9° in **1**) is achieved by narrowing C-S-C-N [90.9° for C(2)S(2)C(21)N(21) as against 104.8° for C(1)S(1)C(11)N(11)] and C-S-C [99.8° for C(2)S(2)C(21) as against 102.8° for C(1)S(1)C(11)], and shows the flexibility of this ligand.

A final noteworthy difference between molecules **1** and **2** concerns the butyl groups. The torsion angles about C(31)–C(32) and C(32)–C(33) are 176.6° and 70.2° respectively, whereas those about C(41)–C(42) and C(42)–C(43) are 163.4° and −178.0° respectively, i.e. in **1** the butyl groups are more compressed than in **2**.

Vibrational spectra

The vibrations of the free ligand in the 4000–600 cm^{-1} range undergo only small shifts upon coordination. The shifts of the imidazole ring stretching vibrations (1600–1300 cm^{-1}) are similar to those previously found upon coordination of imidazole or 2,2′-bisimidazole ligands,[2–5,15–17] and are in all the new complexes, in keeping with the *N*-coordination found in [$SnEt_2Br_2$(bmimt)] and [$SnBu_2Cl_2$(bmimt)] by the X-ray diffraction study.

Table 6 lists selected infrared and Raman data in the range 700–100 cm^{-1}. The two Sn–C vibrations are found at positions close to those found in other complexes of N,N′-bidentate ligands with a *trans* C–Sn–C structure[2–5] (in previous papers a different assignment was proposed for the butyl derivatives in the absence of Raman spectra supporting the assignment now made). The presence of ν_s(Sn–C) in both the IR and Raman spectra of the compounds is in keeping with the non-linearity of C–Sn–C found in the X-ray study of the diethyldibromo and dibutyldichloro derivatives, and together with the Mössbauer data (see below) suggests that C–Sn–C is non-linear in all the new complexes. The *cis*-SnX_2 structure should give rise to two IR and two Raman bands; however, for two compounds there is only a single broad band in the IR spectrum and all the Raman spectra show only very weak bands for which rigorous identification and assignment were not possible.

Table 6 Significant IR and Raman (R) bands in the 700–100 cm^{-1} range[a]

Compound		ν_{as}(Sn–C)	ν_s(Sn–C)	ν(Sn–X)
[$SnMe_2Cl_2$(bmimt)]	IR	576m	497sh	237s,b
	R	—	490s	—
[$SnMe_2Br_2$(bmimt)]	IR	573m	500sh	144s, 131s
	R	—	483s	—
[$SnEt_2Cl_2$(bmimt)]	IR	536m	500m	244s, 233s
	R	523m	507s	—
[$SnEt_2Br_2$(bmimt)]	IR	530m	500m	165s, 148s
	R	—	509s	—
[$SnBu_2Cl_2$(bmimt)]	IR	630w	591w	237s, 222s
	R	629w	592m	—
[$SnBu_2Br_2$(bmimt)]	IR	630w	585m	189s,b
	R	629w	585m	—

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Mössbauer spectra

The Mössbauer data listed in Table 7 are typical of hexacoordinate diorganotin(IV) derivatives in which the two organic groups occupy the apical positions of a nearly regular octahedron. As expected, the isomer shift is greater for the bromo than for the chloro derivatives, and also increases in the order methyl < ethyl < butyl; in fact, the *s*-electron density at the Sn atom is in general more affected by variation of the inductive effect of the alkyl moiety than by variation of the electronegativity of the halogen ion.

The spectrum of [$SnBu_2Cl_2$(bmimt)] was initially fitted with a single doublet, which afforded reasonable spectral parameters and a good χ^2 value. However, as the X-ray study showed the presence of two slightly different tin sites, a two-doublet fit was also performed. Reasonable values were obtained for both the doublets (Table 7), but no

Table 7 Mössbauer spectral parameters collected at 80.0 K

Compound	δ (mm s^{-1})[a]	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})	$A_{2/1}$
$[SnMe_2Cl_2(bmimt)]$	1.62	4.01	0.92	1.23
$[SnMe_2Br_2(bmimt)]$	1.70	4.09	0.95	0.90
$[SnEt_2Cl_2(bmimt)]$	1.73	4.12	0.98	1.04
$[SnEt_2Br_2(bmimt)]$	1.81	4.01	0.95	1.24
$[SnBu_2Cl_2(bmimt)]$[b]	1.75	3.99	0.80	1.16
$[SnBu_2Cl_2(bmimt)]$[c]	1.74	3.83	0.80	1.14
	1.78	4.16	0.80	1.14
$[SnBu_2Br_2(bmimt)]$	1.84	4.02	0.80	1.26

[a] Relative to room-temperature SnO_2.
[b] Single-doublet fitting procedure.
[c] Two-doublet fitting procedure: Γ and $A_{2/1}$ were constrained to have the same value for the two doublets.

significant reduction in the standard deviation of the fit. A similar two-doublet fit for the analogous bromide adduct likewise afforded inconclusive results (not shown). Optimization of the p.q.s. for the nitrogen atoms of $[SnBu_2Cl_2(bmimt)]$ by using the single-doublet results and the experimental bond angles afforded a value very close to that reported for phenanthroline, -0.04 mm s^{-1}, suggesting that the two ligands have similar donor abilities with respect to tin.

The isomer shifts of these compounds are larger than those reported for compounds containing other *N,N′*-bidentate ligands with aromatic nitrogen donor atoms. For instance, the values reported for analogous 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) compounds[18] are about 0.20 mm s^{-1} smaller than those listed in Table 7, although $[SnR_2Cl_2(H_2BIm)]$ (H_2BIm = 2,2′-bisimidazole) and $[SnR_2X_2(MBIm)]$ (MBIm = *N*-methyl-2,2′-bisimidazole)[2,3] have values closer to those obtained in this work.

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.[19]

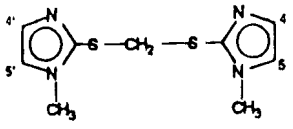
Table 8 lists the chief features of the ^{1}H NMR spectra of the donor and its adducts in $CDCl_3$. Since the methyl complexes are only poorly soluble in $CDCl_3$, spectra were also run in DMSO-d_6, but the results are not included in Table 8 because the chemical shifts and $^2J(^{117/119}Sn–^1H)$ coupling constants in DMSO-d_6 are similar to those of the free donor and acceptor in this solvent. This shows that, as for $[SnR_2X_2(Hmimt)_n]$ complexes (n = 1 or 2),[20,21] the high donor capacity of the solvent leads to its displacing the ligand to form $[SnR_2X_2(DMSO\text{-}d_6)_n]$ compounds. In the weaker donor $CDCl_3$ the chemical shifts and coupling constants of the complexes differ from those of the free acceptor and donor species.

The ^{1}H NMR spectrum of bmimt in $CDCl_3$ is similar to that of the parent ligand Hmimt in the same solvent (3.61s -CH_3; 6.67d, -CH; 6.71d, -CH; 11.36s,b, -NH), except that there is no -NH signal, a

Table 8 ^{1}H NMR parameters (δ in ppm, J in Hz) in $CDCl_3$

Compound	SnR_2	$^nJ(^{119/117}Sn–H)$	N(1)-CH_3	-CH_2-	H(5,5′)	H(4,4′)
bmimt[a]	—	—	3.60(s)	4.61(s)	6.91(d)	7.06(d)
$[SnMe_2Cl_2(bmimt)]$	1.33(s)	87.5/84.4 (n = 2)	3.75(s)	4.50(s)	7.09(s,b)	7.33(s,b)
$[SnMe_2Br_2(bmimt)]$	1.43(s)	74.3/71.1 (n = 2)	3.73(s)	4.63(s)	7.05(d)	7.24(d)
$[SnEt_2Cl_2(bmimt)]$	1.39(t)	161.0/153.9 (n = 3)	3.75(s)	4.43(s)	7.10(d)	7.34(d)
	1.89(q)	73.6/70.5 (n = 2)				
$[SnEt_2Br_2(bmimt)]$	1.40(t)	154.6/147.7 (n = 3)	3.72(s)	4.58(s)	7.08(d)	7.25(d)
	1.96(q)	71.4/68.3 (n = 2)				
$[SnBu_2Cl_2(bmimt)]$	0.88(t)	— [b]	3.71(s)	4.57(s)	7.09(d)	7.23(d)
	1.36(m)					
	1.77(m)					
	1.86(m)					
$[SnBu_2Br_2(bmimt)]$	0.94(t)	— [b]	3.67(s)	4.67(s)	6.98(d)	7.13(d)
	1.42(q)					
	1.80(m)					
	1.90(m)					

[a] Numbering scheme:
[b] Not observed.



new singlet appears at 4.57 ppm due to the -CH_2- group, and the other signals are deshielded. The signals for H(4,4′) and H(5,5′) were assigned on the basis of a NOE experiment. The ^{13}C NMR spectrum was interpreted by means of a ^{1}H–^{13}C HMQC experiment [33.4,-CH_3; 40.0,-CH_2-; 122.8,-C(5,5′); 129.8,-C(4,4′); 140.1,-C(2,2′)]; the C(2,2′) signal shows considerable shielding with respect to C(2) in Hmimt (δ = 160.2 ppm), shifting close to its position in *N*-methyl-2-methylthioimidazole (141.7 ppm)[22] as a consequence of thione-thiol evolution.

In the complexes, the bmimt proton signals are shifted downfield, especially those of H(4) and H(4′), the protons closest to the donor atoms N(3) and N(3′). In general, the deshielding is greater than in the complexes [$SnR_2X_2(Hmimt)_n$] (n = 1, 2),[20,21] in which Hmimt is coordinated via the exocyclic S atom. On the basis of these shifts and the coupling constants, which are larger than those of the free acceptors,[15,16] it may be concluded that in the methyl and ethyl derivatives the Sn–N interaction persists, at least partially, in $CDCl_3$ solution. The low solubility of the butyl complexes prevented analysis of their coupling constants, but the chemical shifts of the bmimt signals in these complexes again suggest that coordination persists in solution.

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