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# Organotin compounds with 2,2′-biimidazole derivatives. The crystal structure of dibromo(*N,N*′-dimethyl-2,2′-biimidazole)dimethyltin(IV)

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## Abstract

The compounds [$SnMe_2Br_2$(DMBIm)], [$(SnMe_2X_2)_2$(DMBIm)] and $(NEt_4)_2[(SnMe_2X_3)_2$(DMBIm)] (X = Cl or Br; DMBIm = *N,N*′-dimethyl-2,2′-biimidazole) have been synthesized and characterized by conductivity measurements and IR and $^1H$ NMR spectroscopy. The structure of dibromo(*N,N*′-dimethyl-2,2′-biimidazole)dimethyltin(IV) was determined by X-ray diffraction. Crystals are: orthorhombic, $P2_12_12_1$, with *a* 9.402(2), *b* 10.389(3), *c* 16.228(3) Å, *V* 1585 Å$^3$, $Z = 4$. The structure was refined to $R = 0.047$ based on 1461 observed intensities. The compound consists of discrete [$SnMe_2Br_2$(DMBIm)] molecules in which the tin atom is octahedrally six-coordinate with *trans* methyl groups and bidentate DMBIm. IR data for [$(SnMe_2X_2)_2$(DMBIm)] complexes are consistent with coordination number 5, and those for $(NEt_4)_2[(SnMe_2X_3)_2$(DMBIm)] with coordination number 6 for the tin atom. The $^1H$ NMR spectra show that the compounds undergo extensive dissociation in $CDCl_3$.

## Introduction

Certain complexes [$SnR_2X_2L$] where L is a bidentate ligand with N donor atoms, are known to possess antitumor activity [1–4]. Crowe *et al.* suggested [4 and references therein] that the presence of Sn–N bonds of length 2.39 Å or more makes this type of complex therapeutically active, whereas those with Sn–N bonds

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less than 2.39 Å are inactive. Consequently detailed structural data for these compounds are called for. At the same time, since all these potential drugs are usually administered in solution, both in *in vitro* and *in vivo* experiments, information about their behavior in solution is also important.

Previously [5] we synthesized $[SnR_2X_2(H_2BIm)]$ and $[(SnMe_2X_2)_2(H_2BIm)]$ (X = Cl or Br; $H_2BIm$ = 2,2′-biimidazole) and carried out a preliminary study of their inhibitory effects on tumor cell division.

Instead of the poorly soluble $H_2BIm$ derivatives, we have now used the more soluble derived from *N,N′*-dimethyl-2,2′-biimidazole DMBIm, studying its interaction with dimethyltin(IV) dihalides. We report here the most relevant results, including the crystal structure of $[SnMe_2Br_2(DMBIm)]$.

## Experimental

### *Materials*

Dimethyltin dichloride and dimethyltin dibromide (Ventron) were used as supplied. Solvents were purified by the usual methods. DMBIm was prepared as described in the literature [6,7].

### *Preparation of compounds*

*[SnMe₂Br₂(DMBIm)].* A solution of DMBIm (1.8 mmol) in 20 ml of $CH_2Cl_2$ was added dropwise to a solution of $SnMe_2Br_2$ (1.8 mmol) in 15 ml of $CH_2Cl_2$. The mixture was stirred and cooled, and the beige crystalline solid formed was filtered off and dried *in vacuo*. Anal. Found: C, 25.0; H, 3.2; N, 11.9. $C_{10}H_{16}Br_2N_4Sn$ calc.: C, 25.5; H, 3.4; N, 11.9%. M.p. 164°C. $\Lambda_M$ 1.4 $ohm^{-1}$ $cm^2$ $mol^{-1}$.

*[(SnMe₂Cl₂)₂(DMBIm)].* A solution of $SnMe_2Cl_2$ (4.8 mmol) in 20 ml of $CH_2Cl_2$ was added dropwise to a solution of DMBIm (2.4 mmol) in 20 ml of $CH_2Cl_2$. Upon stirring, a white solid was formed which was filtered off and dried *in vacuo*. Anal. Found: C, 23.7; H, 3.4; N, 9.5. $C_{12}H_{22}Cl_4N_4Sn_2$ calc.: C, 24.0; H, 3.7; N, 9.3%. M.p. 180°C. $\Lambda_M$ 0.9 $ohm^{-1}$ $cm^2$ $mol^{-1}$. This compound was also obtained from a 1:1 molar mixture of reagents.

*[(SnMe₂Br₂)₂(DMBIm)]*, a beige solid, was prepared by a similar procedure. Anal. Found: C, 18.6; H, 2.7; N, 7.4. $C_{12}H_{22}Br_4N_4Sn_2$ calc.: C, 18.5; H, 2.8; N, 7.2%. M.p. 164°C. $\Lambda_M$ 2.1 $ohm^{-1}$ $cm^2$ $mol^{-1}$.

*(NEt₄)₂[(SnMe₂Cl₃)₂(DMBIm)].* A solution of $[(SnMe_2Cl_2)_2(DMBIm)]$ (0.4 mmol) in 20 ml of MeOH was added to a solution of $NEt_4Cl$ (0.8 mmol) in 20 ml of MeOH. After stirring, the solvent was evaporated off and the white solid obtained was dried *in vacuo*. Anal. Found: C, 34.7; H, 6.7; N, 8.7. $C_{28}H_{62}Cl_6N_6Sn_2$ calc.: C, 36.0; H, 6.7; N, 9.0%. M.p. 75°C. $\Lambda_M$: 350.2 $ohm^{-1}$ $cm^2$ $mol^{-1}$.

*(NEt₄)₂[(SnMe₂Br₃)₂(DMBIm)]*, a white solid, was prepared similarly. Anal. Found: C, 27.9; H, 5.5; N, 7.0. $C_{28}H_{62}Br_6N_6Sn_2$ calc.: C, 28.0; H, 5.2; N, 7.0. M.p. 115°C. $\Lambda_M$ 525.4 $ohm^{-1}$ $cm^2$ $mol^{-1}$.

### *Physical measurements*

Analytical data were obtained with a Perkin–Elmer 240B apparatus. Melting points were determined in a Büchi apparatus. IR spectra (4000–200 $cm^{-1}$) were recorded in Nujol mulls or KBr discs with a Perkin–Elmer 1330 apparatus. Molar

Table 1

Crystal and intensity data for [$SnMe_2Br_2$(DMBIm)]

| | |
|---|---|
| Formula | $C_{10}H_{16}Br_2N_4Sn$ |
| FW | 471 |
| Cell constants | $a = 9.402(2)$ Å |
| | $b = 10.389(3)$ Å |
| | $c = 16.228(3)$ Å |
| | $V = 1585$ Å$^3$ |
| Density (calc.) | $D_c = 1.97$ g cm$^{-3}$ |
| Molecules per cell | $Z = 4$ |
| System | orthorhombic |
| Space group | $P2_12_12_1$ |
| Absorption (Mo-$K_\alpha$) | $\mu = 66$ cm$^{-1}$ |
| Wavelength (Mo-$K_\alpha$) | $\lambda = 0.7107$ Å |
| Scan method | $\theta/2\theta$ |
| $2\theta$ limits | $3° < 2\theta < 50°$ |
| Scan speed | 2°/min |
| Data collected | 1634 |
| Data with $I > 3\sigma(I)$ | 1461 |
| Corrections applied | Lp, absorption [9] |
| Discrepancy factor | $R = 0.047$ |

conductivities ($10^{-3}$ $M$ in acetonitrile) were measured with a WTW LF-3 conductivity meter. $^1$H NMR spectra were recorded with a Bruker WM-250 spectrometer.

### *Determination of the structure*

A crystal of maximum dimension 0.2 mm was selected and used for X-ray analysis. Data were collected on a Philips PW 1100 diffractometer using Mo-$K_\alpha$ radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. The crystals were stable under irradiation. The structure was solved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. All hydrogen atoms were located on the Fourier difference maps, but were generally introduced in calculated positions with fixed C–H distances and isotropic temperature factors (C–H = 0.96 Å, $U_{iso} = 0.08$ Å$^2$). Anisotropy was introduced for all non-hydrogen atoms. Scale factor and positional and thermal parameters were refined by minimizing the function $\Sigma w(\Delta F)^2$, with $w = 1$. At convergence, the largest parameter shift of the refined parameters of the non-hydrogen atoms was 0.2 times the standard deviation. No significant electronic density residue was observed in the final electron density map. Form factors for the atoms were supplied internally by the SHELX program system [8]. Crystal and intensity data, final atomic parameters and bond distances and angles are listed in Tables 1, 2 and 3 respectively. Tables of hydrogen atoms coordinates and structure factors are available from the authors.

## **Results and discussion**

### *Description of the structure*

The crystal structure of [$SnMe_2Br_2$(DMBIm)] is shown in Fig. 1 together with the numbering scheme used. The tin atom is six-coordinate in a rather irregular

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($10^4$) [a]

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Sn | 891(1) | 9566(1) | 8538(1) | 46(1) |
| Br(1) | 3403(2) | 10954(2) | 8564(1) | 66(1) |
| Br(2) | 447(2) | 8588(2) | 10071(1) | 71(1) |
| N(1) | 519(13) | 9952(12) | 7150(7) | 57(4) |
| C(1) | 1412(14) | 10292(14) | 6495(10) | 60(5) |
| C(2) | 717(16) | 10146(14) | 5796(9) | 56(5) |
| C(3) | −1639(18) | 9259(18) | 5394(10) | 77(6) |
| N(2) | −627(14) | 9660(12) | 5999(6) | 55(4) |
| C(4) | −693(14) | 9628(14) | 6828(7) | 46(4) |
| C(5) | −1783(14) | 9127(12) | 7408(8) | 45(4) |
| N(3) | −3199(12) | 9100(11) | 7393(8) | 55(4) |
| C(6) | −4205(16) | 9609(19) | 6804(10) | 75(6) |
| C(7) | −3645(16) | 8606(15) | 8123(9) | 61(5) |
| C(8) | −2451(14) | 8402(13) | 8569(11) | 58(5) |
| N(4) | −1260(10) | 8740(10) | 8136(6) | 42(3) |
| C(9) | −205(16) | 11250(15) | 8893(10) | 65(5) |
| C(10) | 2072(16) | 7899(14) | 8202(10) | 66(6) |

[a] Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

octahedral environment. The four atoms of the base plane are only roughly coplanar, being alternately displaced from the mean plane [Br(1) +0.04, Br(2) −0.04, N(4) +0.07, N(1) −0.07 Å] while Sn lies approximately in the plane [Sn −0.02 Å]. The Sn–C bond lengths are very similar to those found in other bromide compounds [10]. Neither the two Sn–Br bonds nor the two Sn–N bonds are exactly the same length; such non-equivalence of the two M–N distances has also been reported for other complexes of 2,2′-biimidazole or its derivatives [11,12]. The average Sn–N bond lengths, 2.30 Å, is smaller than others reported for tin complexes of bidentate *N*-donor ligands [4, 13 and references therein]. Note that the longer Sn–Br bond is *trans* to the shorter Sn–N bond and *vice versa*. Apart from possible influences of the crystal lattice, the Sn bond angles seem to be affected mainly by the relative bulkiness of the Br anions (Br–Sn–Br ≈ 108°) and by geometrical constraints in the bidentate ligand, which subtends a chelation angle of only 70°, less than in other complexes of this ligand or its derivatives [11,12,14,15].

The two imidazole rings make an angle of 23.8° with each other. The (N(1), N(2))-ring makes an angle of 16.3° with the $Br_2N_2$ plane, and the (N(3), N(4))-ring an angle of 26.1°. As in related systems [12], certain bond angles also show asymmetries induced by coordination: although the internal angles of the rings are very similar and have the expected values [16], the N(1)–C(4)–C(5) and N(4)–C(5)–C(4) angles (mean 115°) are about 18° smaller than the adjacent external angles, whereas this difference is non-existent or much smaller in 2,2′-biimidazoles and its derivatives [17 and references therein]. The angle of 24° between the rings and the observed asymmetries at C(4) and C(5) seem to strike a balance between the effects of steric hindrance between the DMBIm methyl groups, which favour rotation of two rings about the C(4)–C(5) axis, and coordination to the metal ion, which requires a relatively planar ligand and hence coplanar DMBIm rings.

Table 3

Bond lengths (Å) and angles (°) for [$SnMe_2Br_2$(DMBIm)]. E.s.d.'s in parentheses refer to the least significant digit

| | | | |
|---|---|---|---|
| Sn–Br(1) | 2.767(2) | Sn–Br(2) | 2.719(2) |
| Sn–N(1) | 2.32(1) | Sn–N(4) | 2.29(1) |
| Sn–C(9) | 2.11(2) | Sn–C(10) | 2.13(2) |
| N(1)–C(1) | 1.40(2) | N(1)–C(4) | 1.30(2) |
| C(1)–C(2) | 1.32(2) | C(2)–N(2) | 1.40(2) |
| C(3)–N(2) | 1.43(2) | N(2)–C(4) | 1.35(2) |
| C(4)–C(5) | 1.49(2) | C(5)–N(3) | 1.33(2) |
| C(5)–N(4) | 1.34(2) | N(3)–C(6) | 1.44(2) |
| N(3)–C(7) | 1.36(2) | C(7)–C(8) | 1.35(2) |
| C(8)–N(4) | 1.37(2) | | |
| C(9)–Sn–C(10) | 177.7(6) | Br(1)–Sn–C(10) | 89.0(4) |
| Br(1)–Sn–N(4) | 162.3(3) | Br(2)–Sn–C(10) | 90.6(4) |
| Br(2)–Sn–N(1) | 158.7(3) | N(1)–Sn–C(10) | 88.3(5) |
| Br(1)–Sn–C(9) | 88.9(4) | N(4)–Sn–C(10) | 94.7(5) |
| Br(2)–Sn–C(9) | 89.2(4) | N(1)–Sn–N(4) | 69.8(4) |
| N(1)–Sn–C(9) | 92.8(5) | Br(1)–Sn–N(1) | 93.1(3) |
| N(4)–Sn–C(9) | 87.6(5) | Br(1)–Sn–Br(2) | 108.2(1) |
| | | Br(2)–Sn–N(4) | 89.2(2) |
| Sn–N(1)–C(1) | 133.8(9) | Sn–N(4)–C(8) | 132.2(9) |
| Sn–N(1)–C(4) | 118.7(9) | Sn–N(4)–C(5) | 117.5(8) |
| C(1)–N(1)–C(4) | 107(1) | C(5)–N(4)–C(8) | 103(1) |
| N(1)–C(1)–C(2) | 109(1) | N(4)–C(8)–C(7) | 111(1) |
| C(1)–C(2)–N(2) | 107(1) | C(8)–C(7)–N(3) | 106(1) |
| C(2)–N(2)–C(3) | 123(1) | C(7)–N(3)–C(6) | 121(1) |
| C(2)–N(2)–C(4) | 107(1) | C(7)–N(3)–C(5) | 108(1) |
| C(3)–N(2)–C(4) | 130(1) | C(6)–N(3)–C(5) | 131(1) |
| N(2)–C(4)–N(1) | 111(1) | N(3)–C(5)–N(4) | 112(1) |
| N(1)–C(4)–C(5) | 116(1) | N(4)–C(5)–C(4) | 114(1) |
| N(2)–C(4)–C(5) | 132(1) | N(3)–C(5)–C(4) | 133(1) |

The bond lengths in the DMBIm rings are similar to those found in other imidazole and biimidazole complexes [18,11]: the C(1)–N(1), C(2)–N(2), C(8)–N(4) and C(7)–N(3) bonds (mean 1.38 Å) are all longer than the aromatic C–N distance in pyridine, (1.340(1) Å [19]), while C(4)–N(1), C(4)–N(2), C(5)–N(4) and C(5)–N(3) (mean 1.33 Å) are almost equal to this distance. The geometry of these rings as a whole indicates that $\pi$-delocalization affects the N–C bonds, while the C–C bonds (1.33 and 1.35 Å) are clearly double. The C(4)–C(5) distance (1.49 Å) is approximately the length of a normal covalent $C(sp^2)$–$C(sp^2)$ bond (1.479 Å) [20]; it is longer than in other coordinated biimidazole derivatives [11–14], probably as part of the accommodation of the ligand to the requirement of bidentate coordination to Sn.

### *IR spectra*

The small frequency shifts induced by coordination in the most significant ring stretching vibrations (1600–1300 $cm^{-1}$) are similar to those previously reported for imidazole [10] and 2,2'-biimidazole [5] complexes, and are in all cases in keeping with bonding through the pyridine-like nitrogen and with the small structural

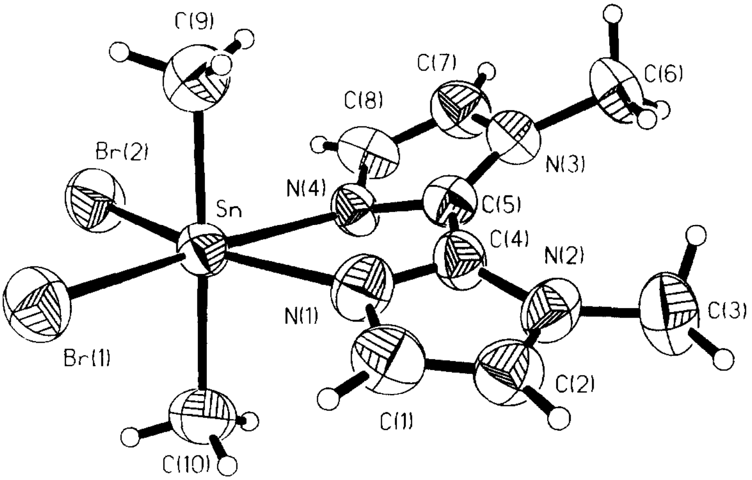


Fig. 1. The crystal structure of [$SnMe_2Br_2$(DMBIm)]

modifications in the imidazole rings observed in [$SnMe_2Br_2$(DMBIm)]. As in 2,2′-biimidazole complexes [5], the 1:1 and 2:1 complexes have IR spectra that differ slightly in the ligand bands, but these differences do not differentiate clearly between bidentate and bridging ligands [11].

Table 4 lists selected infrared data in the 600–200 $cm^{-1}$ range. In the spectrum of [$SnMe_2Br_2$(DMBIm)], in which the X-ray data show the coordination number to be 6 and the C–Sn–C fragment to be linear, $\nu_{as}$ and $\nu_s$(Sn–C) lie at positions and have intensities similar to those found previously for structurally related systems of 2,2′-biimidazole [5]. The tin atom is probably also 6-coordinate in the tetraalkylammonium salts. The positions and intensities of $\nu$(Sn–C) and $\nu$(Sn–Cl) in the spectrum of [$(SnMe_2Cl_2)_2$(DMBIm)] indicate a structural relationship with the analogous compound [$(SnMe_2Cl_2)_2(H_2BIm)$], for which IR and Mössbauer data suggest a coordination number of 5 for the tin atom with $H_2BIm$ acting as a bridging ligand.

*Solutions studies*

The conductivity measurements show that the 1:1 and 2:1 adducts are non-conducting and that the tetraalkylammonium salts strongly ionized in MeCN

Table 4

Selected infrared spectral data for the compounds prepared

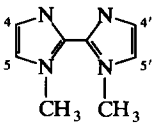
| Compound | $\nu_{as}$(Sn–C) | $\nu_s$(Sn–C) | $\nu$(Sn–X) |
|---|---|---|---|
| [$SnMe_2Br_2$(DMBIm)] | 585vs | 510w | – |
| [$(SnMe_2Cl_2)_2$(DMBIm)] | 570vs | 510s | 320vs |
| | | | 280sh |
| [$(SnMe_2Br_2)_2$(DMBIm)] | 565s | 515m | – |
| $(NEt_4)_2[(SnMe_2Cl_3)_2$(DMBIm)] | 575s | 515m | 310vs |
| | 565s | | 280sh |
| $(NEt_4)_2[(SnMe_2Br_3)_2$(DMBIm)] | 570s,b | 515m | – |

Table 5

$^1$H NMR parameters ($\delta$ in ppm and $J$ in Hz)

| Compound | $\delta(CH_3\text{-}Sn)$ | $^2J(^{117/119}Sn\text{-}^1H)$ | $\delta(CH_3\text{-}CH_2\text{-}N)$ | $\delta$(Ligand) [a] |
|---|---|---|---|---|
| DMBIm | – | – | – | 4.03($CH_3$-N,s)<br>6.95(H5-5′,s)<br>7.11(H4-4′,s) |
| $SnMe_2Cl_2$ | 1.21 | 65.7/68.7 | – | – |
| $SnMe_2Br_2$ | 1.38 | 63.2/66.1 | – | – |
| [$SnMe_2Br_2$(DMBIm)] | 1.36 | 64.2/67.0 | – | 4.04($CH_3$-N,s)<br>6.97(H5-5′,s)<br>7.14(H4-4′,s) |
| [$(SnMe_2Cl_2)_2$(DMBIm)] | 1.21 | 67.3/70 4 | – | 4.03($CH_3$-N,s)<br>7.02(H5-5′,s)<br>7.20(H4-4′,s) |
| [$(SnMe_2Br_2)_2$(DMBIm)] | 1.37 | 64.0/67.0 | – | 4.05($CH_3$-N,s)<br>7.01(H5-5′,s)<br>7.19(H4-4′,s) |
| $(NEt_4)_2$[$(SnMe_2Cl_3)_2$(DMBIm)] | 1.34 | 83.8/87.3 | 1.36(m),3.34(q) | 4.02($CH_3$-N,s)<br>6.99(H5-5′,s)<br>7.13(H4-4′,s) |
| $(NEt_4)_2$[$(SnMe_2Br_3)_2$(DMBIm)] | 1.61 | 77.1/80.6 | 1.39(m),3.40(q) | 4.04($CH_3$-N,s)<br>7.01(H5-5′,s)<br>7.15(H4-4′,s) |

[a] Numbering scheme:



solution [21]. Whereas the molar conductivity of $(NEt_4)_2[(SnMe_2Cl_3)_2(DMBIm)]$ is at the upper limit for a 1:2 electrolyte, the value for the bromide salt (525.4 ohm$^{-1}$ cm$^2$ mol$^{-1}$) is rather higher than this limit, probably due to dissociation of the $[(SnMe_2Br_3)_2(DMBIm)]^{2-}$ anion.

Table 5 shows the $^1$H NMR parameters for the acceptor, the base and their compounds. The values of $^2J(^{117/119}Sn-^1H)$ for the adducts indicate that these compounds are highly dissociated in $CDCl_3$ solution. This explains the very small shifts undergone by the ligand and $SnMe_2$ protons. The values of the coupling constants in the tetraalkylammonium salts are indicative of a higher coordination number for the tin atom; since the DMBIm signals of these derivatives are almost at the same positions as in the free base, the increase in the coordination number must be due to the additional halide ligand, which therefore remains at least partly coordinated to the tin atom in $CDCl_3$ solution, so modifying the Sn–Me signals. Note that the difference in coupling constant between $SnMe_2X_2$ and the anions is bigger in the case of the chlorine derivative, suggesting, in keeping with the conductivity measurements in MeCN solution, that $(SnMe_2Br_3)^-$ is the more prone to dissociation.

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