*Journal of Organometallic Chemistry*, 452 (1993) 47–53

JOM 23310

# Hydrogen bonding in the coordination of *N*- and *S*-donor heterocycles to dialkyltin dihalides. Synthesis and structure of *trans*-dibromodicyclohexylbis(pyrazole-$N^2$)tin(IV), *trans*-dibromodicyclohexylbis(imidazole-$N^3$)tin(IV), and dibutyldichloro[1-methyl-2(3*H*)-imidazolinethione-*S*]tin(IV)

Giuliano Bandoli and Alessandro Dolmella

*Dipartimento di Scienze Farmaceutiche, Università di Padova, via F. Marzolo 5, 35131 Padova (Italy)*

Valerio Peruzzo and Gualtiero Plazzogna

*Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, via F. Marzolo 1, 35131 Padova (Italy)*

(Received September 23, 1992)

## Abstract

Hexacoordinate octahedral crystalline complexes of dicyclohexyltin dibromide with pyrazole (1) and imidazole (2) have been prepared. The X-ray structures have been determined and the effect of the bulkiness of the alkyl groups bonded to the tin on aspects of the structures (such as intra-and inter-molecular hydrogen bonding, orientation of the ligand plane, and Sn–N bond length) is discussed. As an example of a pentacoordinate trigonal bipyramidal complex, the 1:1 adduct of dibutyltin dichloride with 1-methyl-imidazoline-2-thione (3) has been synthesized and its structure studied.

## 1. Introduction

It has been previously shown that the presence of hydrogen bonds [1] characterizes the structures of the organometallic complexes of biological interest [2], $SnR_2X_2 \cdot nL$ ($R = CH_3$ or $CH{=}CH_2$; $X = Cl$ or Br; $n = 1$ or 2; L = *N*- or *S*-donor heterocycle). Since only small R groups are bonded to the tin in such complexes, we considered it worthwhile to examine the effect of bulky groups such as butyl and cyclohexyl on the metal-to-ligand interaction. We have prepared the title compounds, which exhibit 1:1 and 1:2 tin-to-ligand ratios and studied their molecular structures, for comparison with those of the closely related dimethyl- and divinyl-tin complexes.

## 2. Experimental details

Dibutyltin dichloride, dicyclohexyltin dibromide, pyrazole, imidazole and 1-methyl-2-mercaptoimidazole were commercial products, used as received. The solvents were purified by standard procedures.

### 2.1. *trans-Dibromodicyclohexylbis(pyrazole-$N^2$)tin(IV) (1), $[Sn(C_6H_{11})_2Br_2 \cdot 2C_3H_4N_2]$, and trans-dibromodicyclohexylbis(imidazole-$N^3$)tin(IV) (2), $[Sn(C_6H_{11})_2Br_2 \cdot 2C_3H_4N_2]$*

These compounds were prepared crystalline by diffusion of cyclohexane into a solution of $Sn(C_6H_{11})_2Br_2$ and donor (molar ratio 1:2) in dichloromethane; m.p. (1) 107–110°C, (2) > 250°C. Anal. Found: (1) C, 37.3; H, 5.3; N, 9.7; (2) C, 37.2; H 5.4; N, 9.7. $C_{18}H_{30}Br_2N_4Sn$ calc.: C, 37.08; H 5.20; N, 9.61%. IR: (1) 3276s,br $\nu$(NH) 219m $\nu$(SnBr); (2) 3401vw,br and 3275vw,br $\nu$(NH); 212m $\nu$(SnBr) $cm^{-1}$.

---

Correspondence to: Professor V. Peruzzo.

0022-328X/93/$6.00

### 2.2. *Dibutyldichloro[1-methyl-2(3H)-imidazolinethione-S]tin(IV) (3), [Sn($C_4H_9$)$_2$$Cl_2$ · $C_4H_6N_2S$].*

Dibutyltin dichloride and 1-methyl-2-mercaptoimidazole were dissolved in dichloromethane in a molar ratio of 1 : 1. The yellow slush obtained on evaporation of the solvent was redissolved in chloroform, and hexane was added, with formation of two layers. The mixture gave a clear solution upon addition of dichloromethane. A colourless crystalline solid was obtained by diffusion of carbon tetrachloride into this solution; m.p. 71°C. Anal. Found: C, 34.7; H, 5.9; N, 6.7. $C_{12}H_{24}Cl_2N_2SSn$ calc.: C, 34.48; H, 5.80; N, 6.70%. IR: 263s,br cm$^{-1}$ $\nu$(SnCl).

The IR and far-IR spectra were recorded on a Nicolet 5SXC and a FAR 20F vacuum spectrometer, respectively, using KBr pellets and Nujol mulls.

### 2.3. *X-Ray data collection*

The crystals were mounted on a Nicolet Siemens R3m/V automatic diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Automatic counting and least-squares routines were carried out on 50 reflections for each complex to obtain the cell constants given in Table 1. The $\omega$–$2\theta$ scan technique was employed to record the intensities for a unique set of reflections for which $4° < 2\theta < 50°$, with a scan variable from 4.5 to 14.5° min$^{-1}$ in $\omega$. Two check reflections were measured every 100 reflections; they exhibited no significant decay during the data collection. Intensities were corrected for Lorentz and polarization effects and for absorption, using an empirical method based on $\psi$-scans for five reflections with $\chi$ near 90° or 270°.

### 2.4. *Structure solution and refinement*

In each case, the positional parameters of the heavy atoms were determined by the Patterson method and the remaining non-hydrogen atoms were located subsequently by Fourier maps. The refinement (H atoms in their geometrical positions, with a common, variable isotropic thermal factor) was effected by the full-matrix least-squares technique, the function minimized being $\Sigma w \Delta F^2$, with $w^{-1} = \sigma^2(F) + KF$ ($K$ = 0.0136, 0.0050 and 0.0017 for **1**, **2**, and **3**, respectively). In the last stage of the refinement, the Fourier difference map showed no significant peaks (largest peaks: 0.9, 1.0 and 0.7 e Å$^{-3}$ near to the heavy atoms for **1**, **2**, and **3**, respectively). The crystal data and the final $R$ values are listed in Table 1. Atomic scattering factors were taken from ref. 3, and the effects of anomalous dispersion for non-hydrogen atoms were corrected for in the structure factor calculations. Final atomic positional parameters, with e.s.d.s in parentheses, are listed in Table 2, while selected bond distances and angles are reported in Table 3. Additional data, including anisotropic thermal parameters, hydrogen atoms coordinates, bond lengths and angles and observed/calculated structure factors are available from the authors. Data reduction, structure solution and refinement were performed using the SHELXTL-PLUS Programs System [4], and the drawings using the ORTEP program [5].

## 3. Discussion

### 3.1. *Molecular structure of complexes 1 and 2*

Figures 1 and 2 show the molecular structures of **1** and **2** and the atomic numbering scheme employed for

TABLE 1. Crystal data for complexes **1**–**3**

| Complex | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{18}H_{30}Br_2N_4Sn$ | $C_{18}H_{30}Br_2N_4Sn$ | $C_{12}H_{24}Cl_2N_2SSn$ |
| $M$ | 581.0 | 581.0 | 418.0 |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 10.087(4) | 15.295(4) | 10.304(2) |
| $b$ (Å) | 13.019(5) | 8.955(2) | 17.897(3) |
| $c$ (Å) | 25.540(11) | 17.766(4) | 19.684(4) |
| $\beta$ (°) | 101.24(3) | 113.86(2) | 90.62(2) |
| $U$ (Å$^3$) | 3290(2) | 2228(2) | 3630(1) |
| $D_c$ (g cm$^{-3}$) | 1.76 | 1.73 | 1.53 |
| $Z$ | 6 | 4 | 8 |
| $F$(000) | 1716 | 1144 | 1680 |
| Crystal dimensions (mm) | 0.2 × 0.3 × 0.15 | 0.25 × 0.4 × 0.3 | 0.4 × 0.35 × 0.1 |
| Reflections collected | 4244 | 3805 | 4715 |
| Independent reflections ($F_o > 3\sigma\lvert F_o\rvert$) | 2418 | 2390 | 2795 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 47 | 47 | 18 |
| $R(=\Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert)$ | 0.045 | 0.056 | 0.040 |
| $R'[=\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\Sigma w\lvert F_o\rvert^2)]^{1/2}]$ | 0.060 | 0.070 | 0.057 |
| Goodness of fit | 0.50 | 0.90 | 1.12 |

TABLE 2a. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 1

| | *x* | *y* | *z* | *U*[a] |
|---|---|---|---|---|
| Sn(1) | 0 | 5000 | 5000 | 59(1) |
| Sn(2) | 3009(1) | 7668(1) | 7589(1) | 59(1) |
| Br(1) | 245(1) | 5252(1) | 3955(1) | 86(1) |
| Br(2) | 2933(1) | 5674(1) | 7174(1) | 81(1) |
| Br(3) | 3082(1) | 9586(1) | 7990(1) | 90(1) |
| N(1) | −2201(9) | 4334(7) | 4679(4) | 67(4) |
| N(2) | −2797(10) | 4389(7) | 4166(5) | 76(4) |
| N(3) | 5356(9) | 7458(7) | 7917(4) | 66(4) |
| N(4) | 6091(10) | 6636(8) | 7830(5) | 88(5) |
| N(5) | 665(9) | 7776(7) | 7247(5) | 73(4) |
| N(6) | −86(11) | 7077(9) | 6942(5) | 88(5) |
| C(1) | −4113(16) | 4213(11) | 4112(7) | 99(7) |
| C(2) | −4398(15) | 4070(12) | 4599(8) | 104(7) |
| C(3) | −3181(13) | 4145(9) | 4958(6) | 84(6) |
| C(4) | −790(13) | 6561(10) | 4990(6) | 100(6) |
| C(5) | −2136(17) | 6703(12) | 4730(10) | 174(11) |
| C(6) | −2686(17) | 7813(10) | 4692(9) | 136(8) |
| C(7) | −2134(21) | 8438(14) | 5162(8) | 149(10) |
| C(8) | −790(20) | 8324(13) | 5382(9) | 158(10) |
| C(9) | −211(16) | 7226(12) | 5412(8) | 135(9) |
| C(10) | 7387(12) | 6821(11) | 8050(7) | 89(6) |
| C(11) | 7494(14) | 7730(12) | 8250(7) | 94(6) |
| C(12) | 6224(12) | 8138(10) | 8162(6) | 80(5) |
| C(13) | −1347(16) | 7419(16) | 6825(7) | 113(8) |
| C(14) | −1463(15) | 8321(15) | 7052(8) | 119(9) |
| C(15) | −167(12) | 8543(10) | 7339(6) | 81(5) |
| C(16) | 3399(14) | 8237(12) | 6838(6) | 101(7) |
| C(17) | 4706(16) | 8341(17) | 6769(7) | 143(10) |
| C(18) | 4963(15) | 8721(14) | 6230(7) | 120(8) |
| C(19) | 3980(16) | 9419(17) | 5951(8) | 143(10) |
| C(20) | 2664(19) | 9306(17) | 6022(8) | 152(10) |
| C(21) | 2381(14) | 8909(13) | 6529(6) | 107(7) |
| C(22) | 2677(14) | 6926(11) | 8314(5) | 90(6) |
| C(23) | 1357(14) | 6512(14) | 8294(7) | 117(8) |
| C(24) | 1143(18) | 5944(14) | 8800(7) | 118(8) |
| C(25) | 1907(19) | 6336(18) | 9304(8) | 143(10) |
| C(26) | 3233(18) | 6719(12) | 9301(6) | 110(7) |
| C(27) | 3461(16) | 7289(12) | 8820(5) | 106(6) |

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

non-hydrogen atoms. The asymmetric unit of **1** contains two molecules: A, in which an Sn(1) atom is at a centre of symmetry, and B, in a general position. In both molecules the configuration about the tin atom is all-*trans*-octahedral and the equatorial plane can be defined by $N_2C_2$ donor set (through the imino nitrogens of pyrazole molecules and two carbons of cyclohexyl rings), with the bromine atoms at the axial positions [Br–Sn–Br of 180° (symmetry imposed) in A and 179.9° in B]. The Sn(1) atom is in the plane defined by the four ligand atoms N(1), N(1a), C(4), C(4a), while Sn(2) is out from the N(3), N(5), C(16), C(22) plane by 0.09 Å. The two equatorial planes are at a dihedral angle of 73.1°, while the dihedral angle between the two planar pyrazole rings is 0°, symmetrically imposed, in A and 7.3° in B; the cyclohexyl groups, in chair conformation (torsion angles of *ca.* ±35° and atomic mean deviation of ±0.13 Å), are at 0° and 47.5° in A and B, respectively. In general, little departure from the ideal octahedral case can be observed for the angles, the largest deviation being for C(16)–Sn(2)–C(22) (173.5°) and N(3)–Sn(2)–C(22) (87.5°).

The whole structure of **2** is very similar to that of **1**. In the asymmetric unit, consisting of two molecules A and B, centered at ($\frac{1}{2}$, 0, 0) and (0, $\frac{1}{2}$, 0), the tin atoms are of approximately octahedral geometry, the $N_2C_2$ unit defines the equatorial plane and the bromine atoms at apical positions. The two equatorial planes are at a dihedral angle of 71.3° and in both molecules, the dihedral angle between the two strictly planar imidazole rings is symmetrically imposed as 0°. Molecules A and B are virtually superimposable (Fig. 3) (weighted r.m.s. deviation of 0.08 Å, when the fitting is carried out over the octahedra), the only little difference being in the relative orientation of the cyclohexyl/imidazole rings (dihedral angles of 80.1° and 88.4° in A and B, respectively). Briefly, the geometry of **1** and **2** is comparable to that of the all-*trans*-octahedral complexes $SnR_2Br_2 \cdot L_2$ (R = methyl, L =

TABLE 2b. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for 2

| | *x* | *y* | *z* | *U*[a] |
|---|---|---|---|---|
| Sn | 5000 | 0 | 0 | 37(1) |
| Br | 5674(1) | 2303(1) | 1119(1) | 59(1) |
| N(1) | 6406(6) | 220(9) | −270(5) | 49(4) |
| C(2) | 7158(8) | 945(11) | 169(7) | 55(5) |
| N(3) | 7888(7) | 715(11) | −45(7) | 69(5) |
| C(4) | 7556(9) | −205(14) | −690(9) | 75(6) |
| C(5) | 6633(8) | −555(13) | −832(7) | 66(5) |
| C(6) | 5832(9) | −1508(14) | 992(6) | 67(5) |
| C(7) | 6226(10) | −2813(14) | 789(6) | 80(6) |
| C(8) | 6861(8) | −3727(13) | 1474(8) | 72(6) |
| C(9) | 6586(10) | −3872(15) | 2190(7) | 84(6) |
| C(10) | 6142(10) | −2565(13) | 2374(7) | 77(6) |
| C(11) | 5517(8) | −1683(12) | 1676(6) | 60(5) |
| Sn′ | 0 | 5000 | 0 | 36(1) |
| Br′ | 2(1) | 2402(1) | 869(1) | 58(1) |
| N(1′) | −314(6) | 6450(9) | 979(4) | 47(3) |
| C(2′) | −402(8) | 5944(13) | 1640(6) | 61(5) |
| N(3′) | −535(7) | 7113(11) | 2056(5) | 65(4) |
| C(4′) | −519(8) | 8385(15) | 1656(7) | 71(5) |
| C(5′) | −342(8) | 7940(12) | 997(6) | 64(5) |
| C(6′) | 1482(7) | 5339(14) | 713(6) | 67(5) |
| C(7′) | 1886(10) | 4952(21) | 1600(8) | 126(9) |
| C(8′) | 2909(12) | 5345(23) | 2103(9) | 135(9) |
| C(9′) | 3560(12) | 5111(20) | 1730(11) | 124(10) |
| C(10′) | 3202(9) | 5390(19) | 839(9) | 97(7) |
| C(11′) | 2155(9) | 5056(16) | 331(9) | 89(7) |

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

TABLE 2c. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($A^2 \times 10^3$) for **3**

|  | $x$ | $y$ | $z$ | $U$ [a] |
|---|---|---|---|---|
| Sn | 6257(1) | 8689(1) | 823(1) | 48(1) |
| Cl(1) | 8583(2) | 8948(1) | 1096(1) | 60(1) |
| Cl(2) | 3914(2) | 8449(1) | 257(1) | 61(1) |
| S | 6719(2) | 8552(1) | −410(1) | 52(1) |
| N(1) | 9302(8) | 8161(4) | −403(3) | 55(3) |
| N(2) | 8956(8) | 9319(4) | −686(3) | 52(3) |
| C(1) | 8359(8) | 8674(5) | −482(3) | 45(3) |
| C(2) | 10259(10) | 9185(6) | −717(5) | 67(4) |
| C(3) | 10502(9) | 8487(6) | −542(5) | 63(4) |
| C(4) | 8296(9) | 10007(5) | −836(4) | 72(3) |
| C(5) | 6110(10) | 7626(5) | 1314(5) | 78(4) |
| C(6) | 7089(9) | 7414(6) | 1869(4) | 76(3) |
| C(7) | 6967(12) | 7909(7) | 2482(5) | 104(4) |
| C(8) | 7973(12) | 7666(8) | 3020(6) | 135(5) |
| C(9) | 5606(9) | 9781(5) | 1107(5) | 74(4) |
| C(10) | 5735(15) | 9960(10) | 1833(7) | 147(6) |
| C(11) | 5092(13) | 10733(8) | 2109(6) | 134(5) |
| C(12) | 6053(16) | 11260(10) | 1808(7) | 185(7) |
| Sn′ | 1228(1) | 6292(1) | 750(1) | 45(1) |
| Cl(1′) | 3542(2) | 6014(1) | 1037(1) | 62(1) |
| Cl(2′) | −1132(2) | 6559(1) | 200(1) | 61(1) |
| S′ | 1706(2) | 6463(1) | −478(1) | 53(1) |
| N(1′) | 4279(7) | 6873(4) | −438(3) | 55(3) |
| N(2′) | 3970(7) | 5725(4) | −727(3) | 50(3) |
| C(1′) | 3355(8) | 6348(5) | −550(4) | 47(3) |
| C(2′) | 5306(9) | 5865(6) | −741(5) | 64(4) |
| C(3′) | 5457(11) | 6573(6) | −547(5) | 71(4) |
| C(4′) | 3371(9) | 5011(6) | −879(4) | 76(3) |
| C(5′) | 564(9) | 5185(5) | 968(5) | 70(4) |
| C(6′) | 934(12) | 4865(7) | 1659(5) | 108(4) |
| C(7′) | 635(13) | 5322(8) | 2260(6) | 118(4) |
| C(8′) | −708(13) | 5580(8) | 2335(6) | 148(6) |
| C(9′) | 1175(8) | 7358(5) | 1227(4) | 59(3) |
| C(10′) | 1847(11) | 7449(6) | 1870(5) | 84(3) |
| C(11′) | 1927(12) | 8278(7) | 2109(6) | 110(4) |
| C(12′) | 2761(13) | 8402(9) | 2664(7) | 163(6) |

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

TABLE 3a. Selected bond lengths (Å) and angles (°) for **1**

|  |  |  |  |
|---|---|---|---|
| Sn(1)–Br(1) | 2.749(2) | Sn(1)–N(1) | 2.375(9) |
| Sn(1)–C(4) | 2.18(1) | N(1)–N(2) | 1.33(1) |
| N(1)–C(3) | 1.35(2) | N(2)–C(1) | 1.33(2) |
| C(1)–C(2) | 1.34(3) | C(2)–C(3) | 1.38(2) |
| Sn(2)–Br(2) | 2.800(2) | Sn(2)–Br(3) | 2.695(2) |
| Sn(2)–N(3) | 2.368(8) | Sn(2)–N(5) | 2.359(9) |
| Sn(2)–C(16) | 2.16(2) | Sn(2)–C(22) | 2.17(1) |
| N(3)–N(4) | 1.34(1) | N(3)–C(12) | 1.31(1) |
| N(4)–C(10) | 1.34(1) | C(10)–C(11) | 1.28(2) |
| C(11)–C(12) | 1.36(2) | N(5)–N(6) | 1.33(1) |
| N(5)–C(15) | 1.36(2) | N(6)–C(13) | 1.32(2) |
| C(13)–C(14) | 1.32(3) | C(14)–C(15) | 1.40(2) |
| Br(1)–Sn(1)–N(1) | 87.9(3) | Br(1)–Sn(1)–C(4) | 88.8(4) |
| N(1)–Sn(1)–C(4) | 91.2(4) | Sn(1)–N(1)–N(2) | 122.2(8) |
| Br(1)–Sn(1)–Br(1A) | 180.0(1) | N(1)–Sn(1)–Br(1A) | 92.1(3) |
| Sn(1)–N(1)–C(3) | 128.0(9) | N(2)–N(1)–C(3) | 106.9(10) |
| Br(2)–Sn(2)–Br(3) | 180.0(1) | Br(2)–Sn(2)–N(3) | 88.8(2) |
| Br(2)–Sn(2)–N(5) | 87.9(2) | Br(2)–Sn(2)–C(16) | 88.7(4) |
| Br(2)–Sn(2)–C(22) | 85.0(4) | Br(3)–Sn(2)–N(3) | 91.2(2) |
| Br(3)–Sn(2)–N(5) | 92.1(2) | Br(3)–Sn(2)–C(16) | 91.3(4) |
| Br(3)–Sn(2)–C(22) | 94.9(4) | N(3)–Sn(2)–N(5) | 176.6(3) |
| N(3)–Sn(2)–C(16) | 90.6(4) | N(3)–Sn(2)–C(22) | 87.5(4) |
| N(5)–Sn(2)–C(16) | 89.6(5) | N(5)–Sn(2)–C(22) | 91.9(4) |
| C(16)–Sn(2)–C(22) | 173.5(6) | Sn(2)–N(3)–N(4) | 125.4(7) |
| Sn(2)–N(5)–N(6) | 126.2(7) | Sn(2)–N(3)–C(12) | 128.1(8) |
| Sn(2)–N(5)–C(15) | 126.1(7) | N(4)–N(3)–C(12) | 106.1(9) |
| N(6)–N(5)–C(15) | 107.7(9) |  |  |

pyridine [6]; R = methyl [1e], ethyl [1f], or vinyl [1c], L-pyrazole) and the Sn–Br, Sn–C and Sn–N bond distances are in the range of values reported.

As is well known, hydrogen bonding is an important feature of the structure of several diorganotin(IV) halides complexes and the hydrogen-bonding arrangement in **1** and **2** merits some comment. In **1**, as in the previously described pyrazole complexes, this kind of interaction is evident from the IR N–H stretching absorption region [1]. The $\nu$(N–H) absorption band is broader and shifted to lower frequency (compared to that of the uncomplexed monomeric donor. Hamilton [7] has suggested as a criterion of hydrogen bonding that the distance between the hydrogen atoms and possible acceptors should be at least 0.2 Å shorter than the sum of the van der Waals radii. This may be taken to be 3.15 Å for hydrogen and bromine and therefore contacts shorter than 2.95 Å can be considered possible hydrogen bonds. The data for **1** and **2** reported in Table 4 lead to the conclusion that there are two strong hydrogen bonds involving N(3) and N(3′) atoms in **2** (Fig. 4), while much weaker contacts are present in **1**, and, in addition, such interactions are not linear, the

TABLE 3b. Selected bond lengths (Å) and angles (°) for **2**

|  |  |  |  |
|---|---|---|---|
| Sn–Br | 2.758(1) | Sn′–Br′ | 2.792(1) |
| Sn–N(1) | 2.39(1) | Sn′–N(1′) | 2.37(9) |
| Sn–C(6) | 2.18(1) | Sn′–C(6′) | 2.12(9) |
| N(1)–C(2) | 1.28(1) | N(1′)–C(2′) | 1.32(1) |
| N(1)–C(5) | 1.37(2) | N(1′)–C(5′) | 1.34(1) |
| C(2)–N(3) | 1.33(2) | C(2′)–N(3′) | 1.34(2) |
| N(3)–C(4) | 1.33(2) | N(3′)–C(4′) | 1.35(2) |
| Br–Sn–N | 88.8(2) | Br′–Sn′–N(1′) | 90.3(2) |
| Br–Sn–C(6) | 87.4(3) | Br′–Sn′–C(6′) | 91.6(3) |
| N(1)–Sn–C(6) | 86.3(4) | N(1′)–Sn′–C(6′) | 88.2(4) |
| Sn–N(1)–C(2) | 125.5(9) | Sn′–N(1′)–C(2′) | 126.2(7) |
| Sn–N(1)–C(5) | 128.1(7) | Sn′–N(1′)–C(5′) | 125.7(8) |
| C(2)–N(1)–C(5) | 106(1) | C(2′)–N(1′)–C(5′) | 108(1) |
| N(1)–C(2)–N(3) | 113(1) | N(1′)–C(2′)–N(3′) | 108(1) |
| C(2)–N(3)–C(4) | 106(1) | C(2′)–N(3′)–C(4′) | 109(1) |
| N(3)–C(4)–C(5) | 108(1) | N(3′)–C(4′)–C(5′) | 105(1) |
| N(1)–C(5)–C(4) | 107(1) | N(1′)–C(5′)–C(4′) | 109(1) |
| Sn–C(6)–C(7) | 118.2(8) | Sn′–C(6′)–C(7′) | 119.1(9) |
| Sn–C(6)–C(11) | 116.8(8) | Sn′–C(6′)–C(11′) | 118.6(7) |

TABLE 3c. Selected bond lengths (Å) and angles (°) for 3

| | | | |
|---|---|---|---|
| Sn–Cl(1) | 2.493(2) | Sn′–Cl(1′) | 2.494(2) |
| Sn–Cl(2) | 2.683(2) | Sn′–Cl(2′) | 2.694(2) |
| Sn–S | 2.491(2) | Sn′–S′ | 2.491(2) |
| Sn–C(5) | 2.139(9) | Sn′–C(5′) | 2.141(9) |
| Sn–C(9) | 2.143(9) | Sn′–C(9′) | 2.129(8) |
| S–C(1) | 1.711(8) | S′–C(1′) | 1.719(8) |
| N(1)–C(1) | 1.34(1) | N(1′)–C(1′) | 1.35(1) |
| N(1)–C(3) | 1.40(1) | N(1′)–C(3′) | 1.35(1) |
| N(2)–C(1) | 1.37(1) | N(2′)–C(1′) | 1.33(1) |
| N(2)–C(2) | 1.37(1) | N(2′)–C(2′) | 1.40(1) |
| N(2)–C(4) | 1.44(1) | N(2′)–C(4′) | 1.45(1) |
| C(2)–C(3) | 1.32(1) | C(2′)–C(3′) | 1.33(1) |
| Cl(1)–Sn–Cl(2) | 167.8(1) | Cl(1′)–Sn′–Cl(2′) | 169.4(1) |
| Cl(1)–Sn–S | 92.0(1) | Cl(1′)–Sn′–S′ | 92.6(1) |
| Cl(1)–Sn–C(5) | 98.1(3) | Cl(1′)–Sn′–C(5′) | 94.4(3) |
| Cl(1)–Sn–C(9) | 94.4(3) | Cl(1′)–Sn′–C(9′) | 96.2(2) |
| Cl(2)–Sn–S | 76.1(1) | Cl(2′)–Sn′–S′ | 77.0(1) |
| Cl(2)–Sn–C(5) | 88.7(3) | Cl(2′)–Sn′–C(5′) | 87.5(3) |
| Cl(2)–Sn–C(9) | 88.3(3) | Cl(2′)–Sn′–C(9′) | 89.5(2) |
| S–Sn–C(5) | 111.6(3) | S′–Sn′–C(5′) | 112.0(2) |
| S–Sn–C(9) | 114.1(2) | S′–Sn′–C(9′) | 108.9(2) |
| Sn–S–C(1) | 105.5(2) | Sn′–S′–C(1′) | 105.7(3) |
| Sn–C(5)–C(6) | 119.6(7) | Sn′–C(5′)–C(6′) | 116.7(7) |
| Sn–C(9)–C(10) | 115.3(8) | Sn′–C(9′)–C(10′) | 118.3(6) |
| S–C(1)–N(1) | 128.0(7) | S′–C(1′)–N(1′) | 126.8(7) |
| S–C(1)–N(2) | 125.4(7) | S′–C(1′)–N(2′) | 126.5(7) |
| N(1)–C(1)–N(2) | 106.4(7) | N(1′)–C(1′)–N(2′) | 106.7(7) |

bending being as high as 50°. Correspondingly, a dramatic difference in the melting points is observed (107° for 1 and > 250° for 2). These results agree quite well with data found for various other structures containing N ··· Br interactions, in which the distances vary from 3.12 to 3.48 Å (see, *e.g.* [8]). No other unusual short contacts are found in complexes 1 and 2.

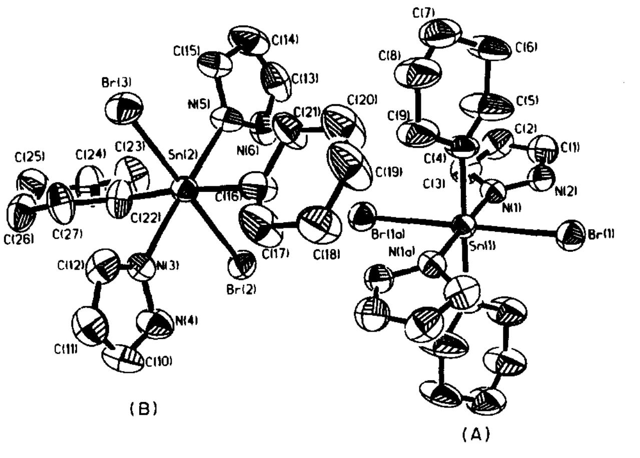

Fig. 1. ORTEP drawing of 1 with atom-numbering scheme and the thermal ellipsoids at the 40% probability level.

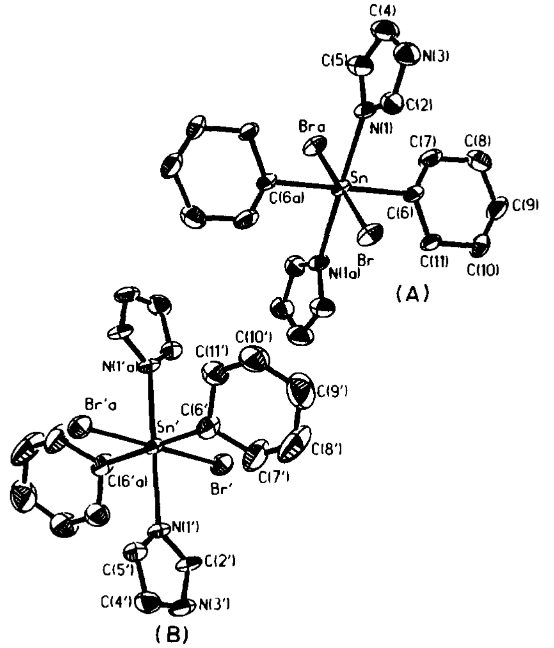

Fig. 2. ORTEP view of compound 2.

### 3.2. Molecular structure of complex 3

The structure of 3, shown in Fig. 5, consists of distorted trigonal-bipyramidal $Sn(n\text{-butyl})_2Cl_2 \cdot (mit)$ molecules (mit = 1-methyl-2(3*H*)-imidazolinethione) held together by two effective and linear hydrogen bonds (Table 4). The asymmetric unit comprises two molecules: A and B, both in general positions. In each molecule, the coordination at Sn may be described as

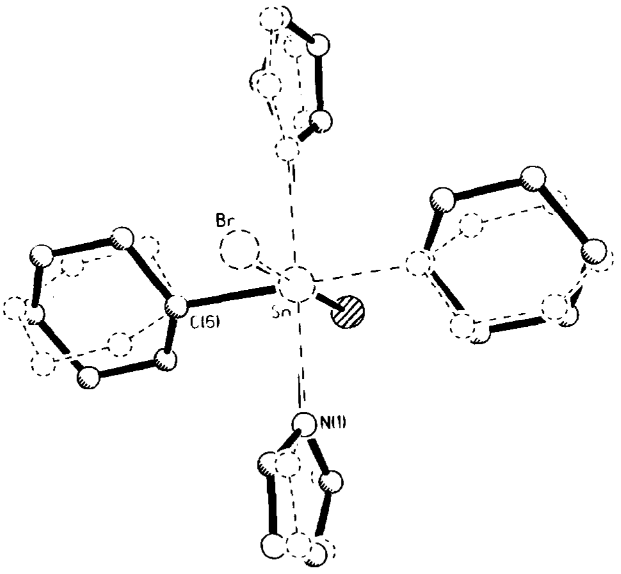

Fig. 3. Superimposition of molecule A (———) and (B) (- - - - -) in 2.

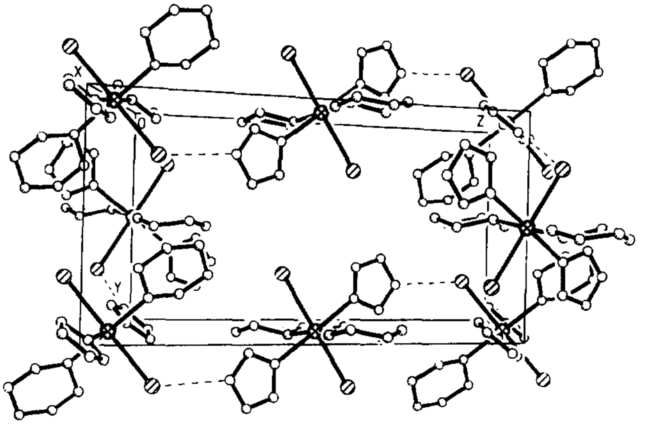

Fig. 4. Packing diagram of **2**; dotted lines show the relevant hydrogen bonded contacts.

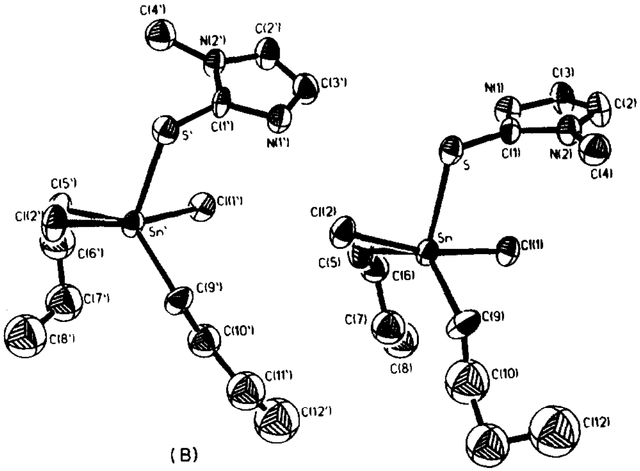

Fig. 5. ORTEP view of compound **3**.

trigonal-bipyramidal with C(5), C(9) (from the alkyl groups) and S in the trigonal plane and the chlorine atoms in the axial positions. The pattern is consistent with the general rule that the more electronegative groups occupy the axial positions of the trigonal bipyramid [9]. Distortion [10] from the ideal trigonal-bipyramidal geometry can be evaluated from the angle formed between the normals to trigonal bipyramid faces that have the common equatorial edge C(5)–C(9): 47.4° in A and 42.6° in B, instead of the idealized value of 53.1°. The geometry about the tin atoms shows that (i) the Cl(2)–Sn–S angles deviate greatly from 90° (76.1° and 77.0° in A and B, respectively); (ii) the bond angles in the trigonal plane are far from 120° (up to 137° for C(5')–Sn'–C(9')) and (iii) Cl–Sn–Cl angles depart from 180° (167.8° and 169.4° in A and B, respectively). Comparison with the analogous complex $Sn(CH_3)_2Br_2 \cdot (mit)$ [11] is of little value. In fact, the Sn–S bond lengths (both 2.491(2) Å) are comparable with 2.47(2) and 2.49(2) Å in $Sn(CH_3)_2Br_2 \cdot (mit)$, as well as the Sn–S–C bond angles (105.5(2)° and 105.7(2)°) are close to the average value for other complexes of mit (107°) [12]. Superimposition of A and B (Fig. 6) shows, as was to be expected, a different orientation of the butyl chains, which assume an *anti*-clinal/*syn*-clinal/*anti*-periplanar and *anti*-periplanar/*anti*-periplanar/*syn*-clinal conformation in A and *anti*-clinal/*syn*-clinal/*syn*-clinal and *anti*-clinal/*anti*-periplanar/*anti*-periplanar in B, as indicated by the values of the torsion angles in SSn–C(5)–C(6)–C(7)C(8) and SSn–C(9)–C(10)–C(11)C(12) sequences, while the fitting of the remaining portion of the molecules is quite good, the weighted r.m.s. deviation being only 0.05 Å.

### 3.3. Conclusions

The bulkiness of the ligands R and X does not significantly affect the coordination and the geometry about the tin, which are certainly much more influenced by L. In fact, whichever R and X, only hexacoordinate octahedral complexes have been crystallized with L = pyrazole or imidazole, whereas with L = mit, a pentacoordinate trigonal-bipyramidal complex was obtained with dimethyl- as well as dibutyl-tin dichloride

TABLE 4. Hydrogen bonding in **1**, **2** and **3**

| Complex | Separation (Å) | | Bond (Å) | | Shortening (Å) | Angle (°) | |
|---|---|---|---|---|---|---|---|
| **1** | N(2) ··· Br(1) | 3.41 | H(2B) ··· Br(1) | 2.78 | 0.37 | N(2)–H(2B) ··· Br(1) | 128 |
| | N(2) ··· Br(2) [a] | 3.40 | H(2B) ··· Br(2) [a] | 2.69 | 0.46 | N(2)–H(2B) ··· Br(2) [a] | 136 |
| | N(4) ··· Br(2) | 3.53 | H(4B) ··· Br(2) | 2.93 | 0.22 | N(4)–H(4B) ··· Br(2) | 126 |
| | N(4) ··· Br(3) [b] | 3.59 | H(4B) ··· Br(3) [b] | 2.91 | 0.24 | N(4)–H(4B) ··· Br(3) [b] | 133 |
| | N(6) ··· Br(2) | 3.50 | H(6C) ··· Br(2) | 2.91 | 0.24 | N(6)–H(6C) ··· Br(2) | 125 |
| **2** | N(3) ··· Br' [c] | 3.33 | H(3A) ··· Br' [c] | 2.46 | 0.69 | N(3)–H(3A) ··· Br' [c] | 175 |
| | N(3'A) ··· Br [d] | 3.34 | H(3'A) ··· Br [d] | 2.45 | 0.70 | N(3')–H(3'A) ··· Br [d] | 166 |
| **3** | N(1') ··· Cl(2) | 3.16 | H(1'A) ··· Cl(2) | 2.28 | 0.72 | N(1')–H(1'A) ··· Cl(2) | 165 |
| | N(1) ··· Cl(2') [e] | 3.14 | H(1A) ··· Cl(2') [e] | 2.24 | 0.76 | N(1)–H(1A) ··· Cl(2') [e] | 171 |

Symmetry codes: [a] $x, 1-y, 1-z$; [b] $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; [c] $1+x, y, z$; [d] $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; [e] $1+x, y, z$.

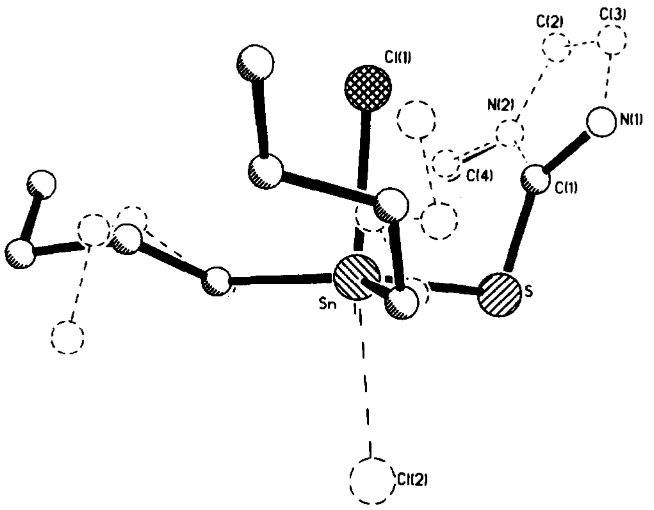

Fig. 6. Superimposition of molecule A (———) and B (— — —) in **3**. The fitted atoms are indicated.

[1,11]. The distortion of the coordination octahedron and the intra- and inter-molecular interaction are only slightly modified. On the other hand, the dihedral angles between the ligand ring plane and the (Sn,N,Br) plane are 14.0° in **1**(A) and 3.2° in **1**(B), and 11.5° in **2**(A) and 2.8° in **2**(B), respectively. These values are much lower than those found for analogous octahedral complexes of the type *trans*-[$Sn(CH_3)_2X_2L_2$]: 26° (L = pyridine) [6], 24° (L = pyrazole) [1b] or 35° (L = imidazole) [1g]. This difference is evidently related to the bulk of the cyclohexyl group. Moreover the Sn–N bonds in the cyclohexyl derivatives are appreciably longer than in the corresponding methyl derivatives with the same L and X = Cl [2.375(9) Å in **1**(A), 2.368(8) and 2.359(9) Å in **1**(B), compared with 2.338(6) Å [1b], and 2.39(1) Å in **2**(A) and 2.37(1) Å in **2**(B), compared with 2.312(2) Å [1g]]. The lengths in the complex with the imidazole are *ca.* 2.39 Å, which is considered the lowest limit for these compounds to give anti-tumor activity [2]. This bond lengthening is probably related to an increase in ionic character as a consequence of the substitution of the methyl by the cyclohexyl and of the chloride by the bromide. In fact the Sn–N bond lengths in **1** and **2** are close to those found in the dibromodiethylbis(pyrazole)tin [2.356(4) Å] [1f].

## References

1 (a) G. Valle, R. Ettorre, U. Vettori, V. Peruzzo and G. Plazzogna, *J. Chem. Soc., Dalton Trans.*, (1987) 815; (b) G. Valle, R. Ettorre, V. Peruzzo and G. Plazzogna, *J. Organomet. Chem., 326* (1987) 169; (c) V. Peruzzo, G. Plazzogna and G. Valle, *J. Organomet. Chem., 375* (1989) 167; (d) R. Graziani, V. Peruzzo, G. Plazzogna and U. Casellato, *J. Organomet. Chem., 396* (1990) 19; (e) B. Alberte, A. S. Gonzales, E. Garcia, J. S. Casas, J. Sordo and E. E. Castelbano, *J. Organomet. Chem., 338* (1988) 187; (f) A. S. Gonzales, B. Alberte, J. S. Casas, J. Sordo, A. Castineiras, W. Hiller and J. S. Strähle, *J. Organomet. Chem., 353* (1988) 169; (g) E. Garcia Martinez, A. Sanchez Gonzalez, A. Macias, M. V. Castaño, J. S. Casas and J. Sordo, *J. Organomet. Chem., 385* (1990) 329.

2 (a) A. J. Crowe and P. J. Smith, *Chem. Ind. (London)*, (1980) 200; (b) A. J. Crowe, P. J. Smith and G. Atassi, *Chem.-Biol. Interact., 32* (1980) 171; (c) A. J. Crowe, P. J. Smith, C. J. Cardin, H. E. Parge and F. E. Smith, *Cancer Lett., 24* (1984) 45; (d) A. K. Saxena and F. Huber, *Coord. Chem. Rev., 95* (1989) 109.

3 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, Vol. 4.

4 G. M. Sheldrick, SHELXTL-PLUS University of Göttingen, Germany, 1987 (Release 4.2, 1990).

5 C. K. Johnson, ORTEP report ORNL-3794, Oak Ridge National Laboratory, Tennessee, USA, 1965.

6 L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin and V. S. Petrosyan, *J. Struct. Chem. (USSR) (Engl. Trans.), 19* (1978) 166.

7 W. C. Hamilton, in E. Rich and N. Davidson (eds.), *Structural Chemistry and Molecular Biology*, Freeman, San Francisco, 1968, p. 446.

8 (a) R. Meulemans, P. Piret and M. Van Meersche, *Acta Crystallogr. Sect. B, 27* (1971) 1420; (b) F. H. Allen, D. Rogers and P. G. H. Troughton, *Acta Crystallogr. Sect. B, 27* (1971) 1325.

9 M. Austin, K. Gebreyes, H. G. Kuivila, K. Swami and J.A. Zubieta, *Organometallics, 6* (1987) 834.

10 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc., 96* (1974) 1748.

11 G. Valle, A. S. Gonzales, U. Vettori and R. Ettorre, *J. Chem. Soc., Dalton Trans.*, (1989) 927.

12 E. S. Raper, J. R. Creighton, D. Robson, J. D. Wilson, W. Clegg and A. Milne, *Inorg. Chim. Acta, 143* (1988) 95.