Crystal Structure and Mass Spectrometry of Dibromodimethyl[1-methyl-2(3*H*)-imidazolinethione-*S*]tin(IV) *

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The structure of $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$ [$C_4H_6N_2S$ = 1-methyl-2(3*H*)-imidazolinethione] consists of trigonal-bipyramidal molecules held together in pairs by two N–H ··· Br hydrogen bonds. The ligand is bonded to the metal through the sulphur atom. The bromine atoms occupy apical positions with a greater Sn–Br bond length for the hydrogen-bonded atom. The mass spectra of $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$ and $Sn(CH_3)_2Cl_2{\cdot}C_4H_6N_2S$ show a much lower tendency for the bromine complex to form ions containing the deprotonated ligand through elimination of hydrogen halide.

Metal co-ordination of heterocyclic thioamides is of current interest especially because of its relevance to metal interactions with biological molecules.[1] This paper reports the crystal structure of the five-co-ordinated tin(IV) complex of 1-methyl-2(3*H*)-imidazolinethione $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$ and the mass spectra of the compound and of its corresponding chloride. We have described previously the six-co-ordinated complex of 2(1*H*)-pyridinethione $Sn(CH_3)_2Cl_2{\cdot}2C_5H_5NS$.[2] The structure of this complex is all-*trans* octahedral with the 2(1*H*)-pyridinethione ligands bonded to the metal through the sulphur atom and the NH hydrogen atoms involved in intramolecular hydrogen bonding with the chloride ligands.

Experimental

Crystals of the complex $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$ were obtained from $CDCl_3$ solutions of $Sn(CH_3)_2Br_2$ and $C_4H_6N_2S$ in the molar ratio 1:1 or 1:2. A well formed crystal of approximate dimensions 0.2 × 0.2 × 0.15 mm was mounted on a Philips PW 1100 diffractometer to determine the cell dimensions and to measure intensity data.

Crystal Data.—$C_6H_{12}Br_2N_2SSn$, M = 422.73, monoclinic, space group *Pa* (no. 7), a = 12.353(2), b = 10.070(2), c = 10.756(2) Å, β = 111.1(3)°, U = 1 248.3 Å^3, Z = 4, D_c = 2.249 g cm^{-3}, $F(000)$ = 792, $\mu(\text{Mo-}K_\alpha)$ = 83.0 cm^{-1}.

Data Collection.—2 516 Independent reflections in the range $4 < 2\theta < 56°$ were collected in the θ—2θ step-scan method using Mo-K_α monochromatized radiation (λ = 0.7107 Å). Reflections with $I > 3\sigma(I)$ were considered as observed (2 048). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination and Refinement of the Structure.—Systematic absences pointed to the centrosymmetric space group $P2_1/a$, but the refinement converged at R = 0.18. The non-centrosymmetric space group *Pa* was then examined and the structure resolved and refined to R = 0.0479 (w = 1). The positions of the Sn and Br atoms were obtained from a three-dimensional Patterson–Fourier synthesis. The remaining non-hydrogen atoms were located in a subsequent electron-density map. The hydrogen atoms were located from a Fourier difference map, but not refined. Final refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. Scattering factors for all atoms were those incorporated in the program SHELX.[3] Positional parameters for the non-hydrogen atoms are listed in Table 1.

Table 1. Fractional co-ordinates for $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$

Atom	x	y	z
Sn(A)	1.0000	0.237 0(5)	1.0000
Br(1A)	0.944 0(7)	0.422 0(9)	1.138 3(9)
Br(2A)	1.060 0(6)	0.065 6(8)	0.824 1(8)
C(6A)	1.194 7(36)	0.248 7(69)	1.110 3(59)
C(7A)	0.875 3(44)	0.105 1(53)	1.010 6(66)
S(2A)	0.960 2(15)	0.374 9(17)	0.798 6(17)
C(1A)	1.120 8(42)	0.631 2(73)	0.943 9(57)
N(1A)	0.982 5(42)	0.634 1(54)	0.901 7(57)
C(2A)	0.923 6(39)	0.531 1(48)	0.843 0(38)
N(3A)	0.799 4(42)	0.566 7(60)	0.803 1(58)
C(4A)	0.803 2(43)	0.687 7(63)	0.842 6(61)
C(5A)	0.915 6(45)	0.733 2(48)	0.916 1(41)
Sn(B)	0.635 6(1)	0.262 6(5)	0.405 6(2)
Br(1B)	0.702 2(7)	0.080 5(8)	0.266 7(9)
Br(2B)	0.578 5(6)	0.437 0(7)	0.575 9(8)
C(6B)	0.465 5(36)	0.247 6(65)	0.288 9(62)
C(7B)	0.775 6(45)	0.409 1(56)	0.414 9(63)
S(2B)	0.678 5(15)	0.124 5(17)	0.609 9(17)
C(1B)	0.523 6(47)	−0.121 6(58)	0.432 4(59)
N(1B)	0.644 2(36)	−0.125 4(45)	0.502 7(44)
C(2B)	0.719 8(49)	−0.027 4(44)	0.575 0(52)
N(3B)	0.819 1(33)	−0.073 8(36)	0.602 5(34)
C(4B)	0.807 2(58)	−0.207 2(44)	0.552 5(70)
C(5B)	0.698 8(63)	−0.239 3(59)	0.498 8(73)

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond distances and angles.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

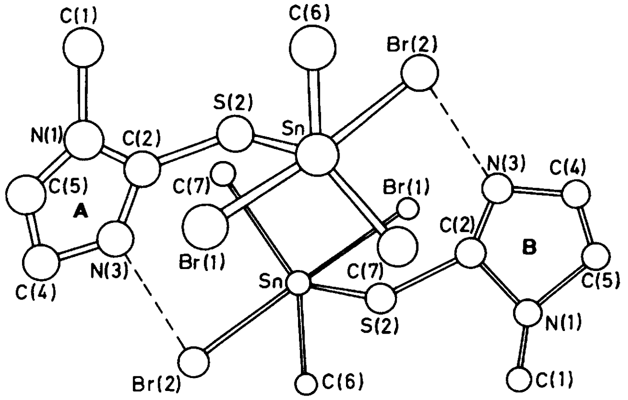

Figure. Perspective drawing of the structure of $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$

Proton N.M.R. Spectra.—Measurements were performed on a JEOL FX-90 spectrometer, with chemical shifts relative to external $SiMe_4$.

Mass Spectra.—Measurements were performed on a VG ZAB 2F spectrometer using an electron-impact (e.i.) source operating at an accelerating voltage of 8 kV and an electron energy of 70 eV (1.12×10^{-17} J) at 200 °C. The collisionally activated decomposition (c.a.d.) spectrum was obtained by colliding ions with air in the second field-free region until there was 50% suppression of the primary beam. The samples were introduced *via* the direct inlet probe in the direct electron impact mode.[4]

Results and Discussion

Crystal Structure.—The structure of the compound is shown in the Figure, and relevant bond lengths and angles are in Table 2. The structure consists of distorted trigonal-bipyramidal $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$ molecules held together in pairs by two N–H $\cdots$ Br hydrogen bonds. The molecules **A** and **B** are related by a pseudo-crystallographic centre of inversion, but their gross features are essentially the same. In each molecule there are two different Sn–Br bond distances, one in the range of values reported for five-co-ordinated organotin(IV) complexes when the bromine atom is in an axial position (2.576—2.739 Å)[5] and the other one significantly longer. Also two different Sn–C bonds are observed in each molecule, but allowance should be made for the uncertainty in the values due to large errors in the positional parameters for the carbon atoms. The observed differences in co-ordination bond lengths can be related to hydrogen bonding with the Br(2) atoms and to non-bonded interactions. Changes of metal–halide bond lengths due to hydrogen bonding have been previously found for compounds of the tetrachlorodimethylstannate(IV) anion.[6] The N–H $\cdots$ Br bond lengths can be compared with those reported for the complex $[Ni(C_4H_6N_2S)_4Br_2]$ (3.218—3.260 Å).[7] Formation of relatively strong hydrogen bonds is consistent with the i.r. spectrum of $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$ showing a characteristic very broad N–H stretching band.

The Sn–S–C bond angles are close to the average value for other complexes of 1-methyl-2(3*H*)-imidazolinethione (107°)[8] and to that found in the octahedral adduct of dimethyltin dichloride with 2(1*H*)-pyridinethione (105.1°).[2] The Sn–S bond lengths in the complexes $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$ (average 2.480 Å) and $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ (2.729 Å)[2] are considerably different. It must be pointed out that metal–sulphur distances observed in the complex $[Cu_2(C_4H_6N_2S)_4][BF_4]_2$[8] are similar to those observed in $[Cu_2(C_5H_5NS)_4]Cl_2$[9] for equivalent bonds. For example, the average Cu–S bond lengths for the monofunctionally bonded ligands are respectively 2.328 Å [1-methyl-2(3*H*)-imidazolinethione] and 2.300 Å [2(1*H*)-pyridinethione]. Therefore, the observed difference of Sn–S bond lengths between the two complexes is ascribed to the different co-ordination number of the metal rather than to different bonding properties of the ligands. The Sn–S bond lengths in the five-co-ordinated complex of $C_4H_6N_2S$ are close to the sum of atomic radii of Sn and S (2.45 Å).[10] The considerably greater value found in the six-co-ordinated complex of C_5H_5NS indicates a much lower degree of covalent character of the Sn–S bonds. Analogous observations have been made previously for Sn–N bonds in six-co-ordinated adducts of heterocyclic ligands.[11,12]

Table 2. Bond lengths (Å) and angles (°) for $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$

	A	B
Sn–Br(1)	2.628(11)	2.674(11)
Sn–Br(2)	2.849(10)	2.806(9)
Sn–C(6)	2.270(40)	2.029(40)
Sn–C(7)	2.068(58)	2.247(58)
Sn–S(2)	2.468(18)	2.491(18)
N(3B) $\cdots$ Br(2A)	3.376(30)	
N(3A) $\cdots$ Br(2B)	3.213(30)	
Br(2)–Sn–Br(1)	171.9(0.3)	173.8(0.3)
C(6)–Sn–Br(1)	96.5(1.7)	93.5(1.9)
C(6)–Sn–Br(2)	84.2(1.7)	90.1(1.9)
C(7)–Sn–Br(1)	94.1(1.8)	95.1(1.7)
C(7)–Sn–Br(2)	91.4(1.9)	86.0(1.7)
C(7)–Sn–C(6)	132.4(2.2)	133.3(2.3)
S(2)–Sn–Br(1)	95.1(0.5)	95.7(0.5)
S(2)–Sn–Br(2)	77.0(0.5)	78.3(0.5)
S(2)–Sn–C(6)	105.6(1.8)	110.4(2.0)
S(2)–Sn–C(7)	119.5(1.6)	114.3(1.5)
C(2)–S(2)–Sn	104.8(1.6)	107.1(2.1)

The ^1H n.m.r. spectra of mixtures of $Sn(CH_3)_2Br_2$ and $C_4H_6N_2S$ in $CDCl_3$ are consistent with co-ordination equilibria. The spectrum of a 0.075 mol dm^{-3} solution of these species displays resonances at δ 1.42 [Sn–CH$_3$, $J(^{119}Sn-^1H) = 69.3$, $J(^{117}Sn-^1H) = 66.3$ Hz], 3.64 (N–CH$_3$), 6.76 (CH), 6.84 (CH), and 11.5 (NH). On addition of 1 equivalent of $C_4H_6N_2S$ the Sn–CH$_3$ resonance is changed to δ 1.45, $J(^{119}Sn-^1H) = 71.4$, $J(^{117}Sn-^1H) = 68.2$ Hz. The resonances are very close to those observed for uncomplexed $C_4H_6N_2S$ at δ 3.59 (N–CH$_3$), 6.67 (CH), 6.71 (CH), and 11.8 (NH), and for $Sn(CH_3)_2Br_2$ at δ 1.37, $J(^{119}Sn-^1H) = 66.1$, $J(^{117}Sn-^1H) = 63.2$ Hz. It is known that slight changes in the proton resonances of 1-methyl-2(3*H*)-imidazolinethione are produced by metal complexation through the sulphur atom.[13] However, a low degree of co-ordination can be inferred from the trend of the tin–proton coupling constants.

Mass Spectra.—The positive-ion mass spectra of $Sn(CH_3)_2Br_2 \cdot C_4H_6N_2S$ and of the analogous chloro-complex are reported in Table 3. Neither spectrum shows the presence of the molecular ion due to fast fragmentation of these species under e.i. conditions and/or thermal decomposition. The low abundance of complex ions of 1-methyl-2(3*H*)-imidazolinethione in both spectra is consistent with extensive dissociation of metal–sulphur bonds. The spectra of the bromo- and chloro-complexes are significantly different. The spectrum of the bromo-complex is characterized by the presence of three complex ions containing the undissociated $C_4H_6N_2S$ ligand and a single ion containing the deprotonated ligand, whereas the spectrum of the chloro-complex displays several ions containing the $C_4H_5N_2S$ group, but no complex ions containing the undissociated ligand. The appearance of the ion $HBr^{\bullet +}$

Table 3. Positive ion mass spectra of $Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$ and $Sn(CH_3)_2Cl_2{\cdot}C_4H_6N_2S$*

$Sn(CH_3)_2Br_2{\cdot}C_4H_6N_2S$: *m/z* 403 [0.37, $Sn(CH_3)Br_2{\cdot}C_4H_6N_2S$], 339 [0.23, $Sn(CH_3)_2Br{\cdot}C_4H_6N_2S$], 323 [0.3, $Sn(CH_3)Br{\cdot}C_4H_5N_2S$], 304 [2.2, $Sn(CH_3)_2Br_2$], 289 [100, $Sn(CH_3)Br_2$], 225 [35.1, $Sn(CH_3)_2Br$], 195 (70.2, SnBr), 114 (84.2, $C_4H_6N_2S$), 80 (4, HBr), 79 (3, Br)

$Sn(CH_3)_2Cl_2{\cdot}C_4H_6N_2S$: *m/z* 294 [0.4, $Sn(CH_3)_2Cl{\cdot}C_4H_5N_2S$], 279 [0.8, $Sn(CH_3)Cl{\cdot}C_4H_5N_2S$], 264 [0.6, $SnCl{\cdot}C_4H_5N_2S$], 259 [0.3, $Sn(CH_3)_2{\cdot}C_4H_5N_2S$], 229 (1, $Sn{\cdot}C_4H_5N_2S$), 216 [2.1, $Sn(CH_3)_2Cl_2$], 201 [48.4, $Sn(CH_3)Cl_2$], 181 [16.2, $Sn(CH_3)_2Cl$], 166 [4.5, $Sn(CH_3)Cl$], 151 (24.7, SnCl), 114 (100, $C_4H_6N_2S$), 36 (4, HCl), 35 (1, Cl)

* Nominal values of *m/z* calculated by considering the isotopes ^{116}Sn, ^{79}Br, and ^{35}Cl. Relative abundances were calculated by summing all the isotopic contributions. Fragment ions of $C_4H_6N_2S$ are not quoted.

Table 4. M.i.k.e. and c.a.d. spectra of the ion $[Sn(CH_3)Br_2{\cdot}C_4H_6N_2S]^+$ *m/z* = 403

Ion	*m/z* [a]	m.i.k.e. [b]	c.a.d. [b]
$SnBr_2{\cdot}C_4H_6N_2S$	388	25	50
$Sn(CH_3)Br{\cdot}C_4H_5N_2S$	323	100	100
$SnBr{\cdot}C_4H_6N_2S$	309	1	10
$Sn(CH_3)Br_2$	289	30	60
$Sn{\cdot}C_4H_6N_2S$	230		10
SnBr	195		10
$C_4H_6N_2S$	114		5

[a] Nominal values calculated by considering the isotopes ^{116}Sn and ^{79}Br. [b] Relative abundances calculated by summing all the isotopic contributions.

or $HCl^{\cdot +}$ and the composition of the tin ions containing the deprotonated ligand show that these species are formed through elimination of hydrogen bromide or chloride involving hydrogen transfer from the N(3) atom to an X atom. Accordingly, the difference between the two spectra is accounted for by the lower tendency of co-ordinated bromide with respect to chloride to undergo intramolecular hydrogen-bonded interaction with the ligand.

Mass analyzed ion kinetic energy (m.i.k.e.) and collisionally activated decomposition (c.a.d.) spectra of the metastable primary ion $Sn(CH_3)Br_2{\cdot}C_4H_6N_2S^+$ are reported in Table 4. The presence in both spectra of the most abundant ion $Sn(CH_3)Br{\cdot}C_4H_5N_2S^+$ confirms that the elimination of hydrogen halide observed in the e.i. spectra of the bromo- and chloro-complexes takes place through ion fragmentation rather than by thermal decomposition of the compounds. The m.i.k.e. and c.a.d. spectra also display ions formed by loss of either CH_3 or $C_4H_6N_2S$ from the metastable ion. The increased abundance of these ions relative to the ion $Sn(CH_3)Br{\cdot}C_4H_5N_2S^+$ in the c.a.d. spectrum demonstrates that elimination of hydrogen bromide is the process with lowest activation energy.[14]

Predominant formation of ions containing the deprotonated ligand has been found also in the mass spectrum of the 2(1*H*)-pyridinethione complex $Sn(CH_3)_2Cl_2{\cdot}2C_5H_5NS$,[2] with relative abundance much higher than in the 1-methyl-2(3*H*)-imidazolinethione complexes. The more facile elimination of hydrogen halide from the six-co-ordinated complex can be accounted for by a greater extent of intramolecular hydrogen bonding with two heterocyclic ligands and to lower metal–halide bond strength. Among other relevant factors is the possibility of changes to the binding mode of the ligands upon deprotonation.[2]

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References

1 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
2 G. Valle, R. Ettorre, U. Vettori, V. Peruzzo, and G. Plazzogna, *J. Chem. Soc., Dalton Trans.*, 1987, 815.
3 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
4 P. Traldi, U. Vettori, and F. Dragoni, *Org. Mass Spectrom.*, 1982, **17**, 587.
5 G. van Koten, J. G. Noltes, and A. L. Spek, *J. Organomet. Chem.*, 1976, **118**, 183; G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, W. M. G. F. Pontenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, 1978, **100**, 5021; L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, and V. S. Petrosyan, *J. Struct. Chem.* (*Engl. Transl.*), 1978, **19**, 269; G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, G. J. Verhoeckx, A. L. Spek, and J. Kroon, *J. Chem. Soc., Dalton Trans.*, 1980, 1352; H. Weichmann, C. Mügge, A. Grand, and J. B. Robert, *J. Organomet. Chem.*, 1982, **238**, 343; J. T. B. H. Jastrzebski, G. van Koten, C. T. Kaap, A. M. M. Schreurs, J. Kroon, and A. L. Spek, *Organometallics*, 1986, **5**, 1551.
6 G. Valle, A. Sánchez González, R. Ettorre, and G. Plazzogna, *J. Organomet. Chem.*, 1988, **348**, 49.
7 R. E. Oughtred, E. S. Raper, and I. W. Nowell, *Inorg. Chim. Acta*, 1984, **84**, L5.
8 E. S. Raper, J. R. Creighton, D. Robson, J. D. Wilson, W. Clegg, and A. Milne, *Inorg. Chim. Acta*, 1988, **143**, 95.
9 E. C. Constable and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1987, 2281.
10 J. C. Slater, *J. Chem. Phys.*, 1964, **41**, 3199.
11 R. Bardi, A. M. Piazzesi, R. Ettorre, and G. Plazzogna, *J. Organomet. Chem.*, 1984, **270**, 171.
12 V. G. Kumar Das, K. M. Lo, Chen Wei, and T. C. W. Mak, *Organometallics*, 1987, **6**, 10.
13 E. S. Raper, M. E. O'Neill, and J. A. Daniels, *Inorg. Chim. Acta*, 1980, **41**, 145.
14 R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.

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