Crystal Structure and Mass Spectrometry of Dichlorodimethylbis[2(1*H*)-pyridinethione-*S*]tin(IV) *

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The structure of the complex $Sn(CH_3)_2Cl_2{\cdot}2C_5H_5NS$ has been determined by single-crystal *X*-ray diffraction methods. The compound crystallizes in the monoclinic system, space group $P2_1/n$, with unit-cell dimensions a = 16.793(5), b = 6.201(3), c = 7.882(3) Å, β = 90.4(3)°, and Z = 2. The configuration about the tin atom is all-*trans* octahedral. The C_5H_5NS ligands are bonded to the metal through the S atom. The observed C(2)–S bond length [1.730(9) Å] is consistent with *ca.* 35% double-bond character, compared to *ca.* 55% for the uncomplexed ligand. The H atoms on the N atoms are involved in intramolecular hydrogen bonding with the chloride ligands, N–H ··· Cl 3.199(9) Å. Mass spectra of $Sn(CH_3)_2Cl_2{\cdot}2C_5H_5NS$ show that facile elimination of HCl from the complex occurs to give a series of ions containing the ligand C_5H_4NS; these can be formulated as complexes of the 2-pyridinethiolate anion, probably bonded through the S atom. Mass spectra of the metastable ion $[Sn(CH_3)Cl(C_5H_4NS)]^+$ show that the Sn–L bond strengths are in the order L = methyl < chlorine < 2-pyridinethiolate.

The co-ordinating properties of alkyltin(IV) halides are of interest particularly because of their relevance to organotin interactions with biological systems.[1] This paper reports studies on the crystal structure and mass spectra of the 1:2 adduct of dimethyltin dichloride and 2(1*H*)-pyridinethione, $Sn(CH_3)_2Cl_2{\cdot}2C_5H_5NS$. The ligand is a model compound for cyclic molecules containing the –NH–C(S)– group (*e.g.* sulphur derivatives of purine and pyrimidine bases). Complexes of 2(1*H*)-pyridinethione and of the 2-pyridinethiolate anion with several metal ions have been described.[2,3] Metal binding takes place predominantly through the S atom for the neutral ligand and through both S and N atoms for the deprotonated molecule. The crystal structure of dichlorobis(2-pyridinethiolato)tin(IV) has been reported.[4] This chelated complex has a distorted octahedral structure with *trans* chlorine but *cis* nitrogen atoms. Preparative and spectroscopic studies of the complexes $SnR_2(C_5H_4NS)_2$,[5] $SnR_2Cl_2{\cdot}2C_5H_5NS$,[6] and $SnCl_4{\cdot}2C_5H_5NS$[7] have also been reported.

Experimental

Crystals of the compound were obtained by addition of cyclohexane to a solution of $Sn(CH_3)_2Cl_2$ and the ligand in the molar ratio of 1:2 in methylene dichloride. A well formed crystal of approximate dimensions 0.2 × 0.3 × 0.6 mm was mounted on a Philips PW 1100 diffactometer to determine the cell dimensions and to measure intensity data.

Crystallography.—Crystal data. $C_{12}H_{16}Cl_2N_2S_2Sn$, M = 441.8, monoclinic, space group $P2_1/n$, a = 16.793(5), b = 6.201(3), c = 7.882(3) Å, β = 90.4(3)°, U = 820.8 Å^3, Z = 2, D_c = 1.788 g cm^{-3}, $F(000)$ = 436, μ(Mo-K_α) = 19.6 cm^{-1}.

Data collection. 1 545 (1 443 unique, R = 0.04) Reflections in the range 2 < 2θ < 50° were collected in the θ—2θ step-scan method using Mo-K_α monochromated radiation (λ = 0.7107 Å). Reflections with $I > 3\sigma(I)$ were considered as observed (1 293). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination and refinement of the structure. The positions of the chlorine 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. Final refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The final conventional R factor was 0.0436 (w = 1). Scattering factors for all atoms were those incorporated in the program SHELX.[8] Positional parameters for the non-hydrogen atoms are listed in Table 1.

Mass Spectra.—Measurements were performed on a VG 2AB 2F spectrometer. All experiments were conducted using an electronic impact (e.i.)–chemical ionization (c.i.) source operating at 8 kV accelerating voltage and 70 eV electron energy at 200 °C. The negative-ion mass spectrum was obtained with the c.i. source configuration by introducing the sample together with a 1:1 mixture of CH_4 and $CHCl_3$, producing *ca.* 5 × 10^{-6} mbar (5 × 10^{-4} Pa) pressure into the source housing. 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 sample was introduced *via* the direct inlet probe heated at 120 °C.

Results and Discussion

Crystal Structure.—The structure of the compound is shown in the Figure with the atom-numbering scheme. Bond distances and angles are listed in Table 2. The structure is centro-

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Fractional co-ordinates of the complex $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	0.0000	0.0000	1.0000
Cl	0.076 9(1)	0.223 8(4)	1.231 1(2)
N(1)	0.088 9(5)	−0.150 1(13)	0.580 0(8)
S(1)	0.075 2(1)	0.220 8(4)	0.748 0(2)
C(1)	−0.090 2(7)	0.234 3(19)	0.994 0(12)
C(2)	0.126 6(5)	0.026 9(15)	0.635 1(9)
C(3)	0.206 4(5)	0.047 4(18)	0.592 1(11)
C(4)	0.243 4(6)	−0.112 0(19)	0.499 7(11)
C(5)	0.201 4(6)	−0.290 2(18)	0.446 6(11)
C(6)	0.123 7(6)	−0.306 6(17)	0.488 9(11)

Table 2. Bond distances (Å) and angles (°)

Co-ordination bonds			
Sn–Cl	2.623(2)	Cl–Sn–Cl′	180
Sn–S(1)	2.729(2)	C(1)–Sn–Cl	90.1(3)
Sn–C(1)	2.099(9)	C(1)–Sn–Cl′	89.9(3)
S(1)–Sn–S(1′)	180	C(1)–Sn–C(1′)	180
S(1)–Sn–Cl	90.7(1)	C(1)–Sn–S(1)	88.5(3)
S(1)–Sn–Cl′	89.3(1)	C(1)–Sn–S(1′)	91.5(3)
2(1*H*)-Pyridinethione			
S(1)–C(2)	1.730(9)	Sn–S(1)–C(2)	105.1(3)
C(3)–C(4)	1.378(14)	S(1)–C(2)–C(3)	123.2(7)
N(1)–C(2)	1.338(11)	C(3)–C(4)–C(5)	120.3(9)
C(4)–C(5)	1.375(15)	C(2)–N(1)–C(6)	124.0(8)
N(1)–C(6)	1.344(12)	N(1)–C(2)–C(3)	116.8(8)
C(5)–C(6)	1.353(14)	C(4)–C(5)–C(6)	118.7(9)
C(2)–C(3)	1.391(11)	S(1)–C(2)–N(1)	120.0(6)
		C(2)–C(3)–C(4)	120.1(9)
		N(1)–C(6)–C(5)	120.1(10)
Hydrogen bond			
N(1) · · · Cl′	3.199(9)		

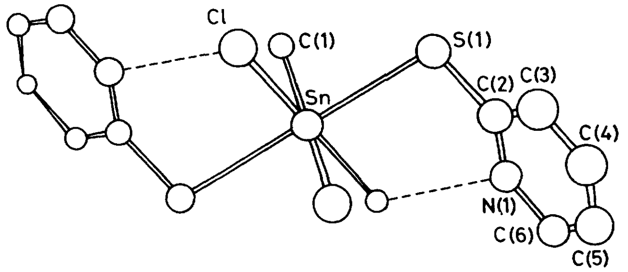

Figure. Perspective drawing of the structure of $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$

symmetric at the tin atom. The co-ordination geometry is all-*trans* octahedral. The bond angles C–Sn–Cl, C–Sn–S, and Cl–Sn–S are close to 90°. The Sn–C and Sn–S bond distances are in the range of values reported for other *trans*-octahedral adducts of $Sn(CH_3)_2Cl_2$.[9–12] The C_5H_5NS ligands are bonded to the metal through the sulphur atom. The pyridine ring is planar, with no atom deviating from the least-squares plane by more than 0.006(9) Å. The deviation of the sulphur atom from this plane is 0.03(1) Å. The observed C(2)–S bond length [1.730(9) Å] can be compared with those reported for the free ligand [1.68(2) Å][13] and for the complexes $[Co(C_5H_5NS)_2Cl_2]$ [1.720(3) Å][14] and $[Cu(C_5H_5NS)_3]NO_3$ [1.68(2) and 1.70(2) Å].[15] Lengthening of the C(2)–S bond upon complexation is consistent with an increased contribution of the zwitterionic resonance form of the ligand, due to stabilization of the negative charge on the S atom. From a proposed relationship between the order and length of carbon–sulphur bonds,[16] the C(2)–S bond in the present compound is assigned *ca.* 35% double-bond character, compared to *ca.* 55% for uncomplexed 2(1*H*)-pyridinethione. This bond length is also similar to the C(2)–S bond lengths in the complex dichlorobis(2-pyridinethiolato)-tin(IV) [1.751(12) and 1.729(12) Å],[4] corresponding to about 25 and 35% double-bond character respectively. However, the Sn–S bond lengths in the chelated complex [2.462(3) and 2.467(3) Å] are significantly shorter than in the present compound. Bond angles and lengths in the pyridine rings in $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ are in agreement with those found in the complex $[Co(C_5H_5NS)_2Cl_2]$; significant differences from uncomplexed 2(1*H*)-pyridinethione[13] are related to an increased aromatic character of the co-ordinated ligand.[14]

The H atoms on the N atoms are involved in intramolecular hydrogen bonding with chloride ligands (see Figure). The observed *d*(N–H · · · Cl) of 3.199(9) Å is close to the shortest N–H · · · Cl distances reported for salts of the type $A_2[SnCl_6]$, $A_2[Sn(CH_3)_2Cl_4]$, and $A[Sn(CH_3)_2Cl_3]$.[17] This is consistent with the characteristic very broad N–H stretching absorption in the i.r. spectrum of the compound, like that observed for other hydrogen-bonded species, *e.g.* $[NHEt_3]Cl$.[18]

The configuration of $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ is comparable to that of the all-*trans* octahedral complex dichlorodimethyl-bis(pyridine *N*-oxide-*O*)tin(IV).[19] The angle Sn–O–N in this complex is 117(1)° and the angles between the normal to the plane of the pyridine ring and the normals to the planes (O, Sn, Cl), (C, Sn, Cl), and (O, Sn, C) are 66.6, 149.0, and 79.2°, respectively. The angles between the normal to the plane of the pyridine ring and the normals to the planes (S, Sn, Cl), (C, Sn, Cl), and (S, Sn, C) in $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ are 59.5, 135.7, and 63.3°. Comparison of data shows that the orientation of the similar pointed ligands in the two complexes is not very different, suggesting that hydrogen bonding and non-bonded interactions in the 2(1*H*)-pyridinethione complex are co-operative rather than opposing conformational factors.

Mass Spectra.—Positive- and negative-ion mass spectra of $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$ are reported in Table 3. Neither spectrum shows the presence of the molecular ions, due to fast fragmentation of these species under e.i. conditions and/or to thermal decomposition of the complex. Extensive dissociation of Sn–(C_5H_5NS) bonds is shown by the presence of a strong signal of the ion $[C_5H_5NS]^{\cdot +}$. This indicates a relatively low tin–sulphur bond strength in the complex. The observed abundances of fragment ions in the positive-ion mass spectrum confirm the effects of the odd or even bonding-electron character on the stability of alkyltin ions.[20] The negative-ion mass spectrum is characterized by a lack of extensive fragmentation processes. It can be noted that the observed negative ions correspond to some of the most abundant ions in the positive mass spectrum, indicating a high stability of these species (*e.g.* m/z = 276). An exception is the formation of the very stable ion $[C_5H_4NS]^-$ instead of $[C_5H_5NS]^{\cdot -}$.

The positive-ion spectrum displays a single tin ion of low abundance containing the C_5H_5NS ligand (m/z = 292) and a series of ions containing the ligand C_5H_4NS. The species with two C_5H_4NS do not possess chlorine atoms, while those with one C_5H_4NS have one or no chlorine atom. These results, together with the appearance of an intense signal due to $[HCl]^{\cdot +}$, indicate a facile elimination of hydrogen chloride from the complex. The resulting ions can be formulated as tin complexes of S-bonded deprotonated thiopyridone. The formation of these species is driven by the preformed N–H · · · Cl interaction in the complex as well as by the increase in Sn–S bonding after ligand deprotonation. Alternative

Table 3. Positive- and negative-ion mass spectra of $Sn(CH_3)_2Cl_2 \cdot 2C_5H_5NS$

Ion	m/z^a	Postive-ion mass spectrum[b]	Negative-ion mass spectrum[b]
$[Sn(CH_3)(C_5H_4NS)_2]$	351	1.5	0.8
$[Sn(C_5H_4NS)_2]$	336	3	
$[Sn(CH_3)_2Cl(C_5H_5NS)]$	292	1.5	
$[Sn(CH_3)_2Cl(C_5H_4NS)]$	291	3	
$[Sn(CH_3)Cl(C_5H_4NS)]$	276	71	100
$[SnCl(C_5H_4NS)]$	261	20	
$[Sn(CH_3)_2(C_5H_4NS)]$	256	12	
$[Sn(C_5H_4NS)]$	226	44	
$[Sn(CH_3)_2Cl_2]$	216	12	
$[Sn(CH_3)Cl_2]$	201	100	17
$[Sn(CH_3)_2Cl]$	181	34	3
$[Sn(CH_3)Cl]$	166	8	
$[SnCl]$	151	70	
$[Sn(CH_3)]$	131	9	
Sn	116	14	
	113	6	
	112	10	
$[C_5H_5NS]$	111	99	
$[C_5H_4NS]$	110	13	10
	84	6	
	83	9	
	82	5	
	81	3	
	79	4	
$[C_5H_4N]$	78	30	
	69	4	
	68	4	
$[C_4H_5N]$	67	93	
	51	23	
	36	15	

[a] Nominal values calculated by considering the isotopes ^{116}Sn and ^{35}Cl. [b] Relative abundances are calculated by summing all the isotropic contributions.

structures for the fragment ions where the anionic ligand acts as a N-donor, or as N,S-donor chelate, cannot be ruled out. Reported structures for $SnCl_2(C_5H_4NS)_2$[4] and other octahedral metal complexes[3] of the chelating anion show S–M–N bond angles of about 66°. From this value it can be inferred that chelate-ring formation is possible also for trigonal-bipyramidal or square-pyramidal configurations at the tin atom, but unlikely for trigonal or tetrahedral ones.

Metastable ion kinetic energy (m.i.k.e.) and c.a.d. spectra of the $[Sn(CH_3)Cl(C_5H_4NS)]^+$ ions have been recorded (Table 4). The m.i.k.e. spectrum represents the collection of ions generated by this species through spontaneous decomposition reactions possessing low activation energies.[21] It shows that the preferred decomposition process is the loss of methyl groups, as previously observed from mass spectra of tetrahedral methylchlorotin(IV) complexes.[22] Of the other two possible primary fragmentations, involving Sn–Cl and Sn–(C_5H_4NS) bond breaking, only the first one takes place. On increasing the internal energy of the decomposing $[Sn(CH_3)Cl(C_5H_4NS)]^+$ ions by collision with air (c.a.d–m.i.k.e. spectrum), the primary ion $[Sn(CH_3)Cl]^{\cdot +}$, formed by loss of C_5H_4NS, becomes observable together with the other primary fragments and several ions due to consecutive fragmentations. The above observations are consistent with Sn–L bond strengths of the ion $[Sn(CH_3)Cl(C_5H_4NS)]^+$ in the order L = methyl < chlorine < 2-pyridinethiolate.

Table 4. M.i.k.e. and c.a.d. spectra of the ion $[Sn(CH_3)Cl(C_5H_4NS)]^+$ (m/z 276)

Ion	m/z^a	m.i.k.e.[b]	c.a.d.[b]
$[SnCl(C_5H_4NS)]^+$	261	100	100
$[Sn(CH_3)(C_5H_4NS)]^+$	241	4	2.5
$[Sn(C_5H_4NS)]^+$	226	1.5	48
$[Sn(CH_3)Cl]^+$	166		3
$[SnCl]^+$	151	7	26
$[Sn(CH_3)]^+$	131		1
Sn^+	116		2

[a] Nominal values calculated by considering the isotopes ^{116}Sn and ^{35}Cl. [b] Relative abundances calculated by summing all the isotopic contributions.

References

1 A. J. Crowe and P. J. Smith, *Chem. Ind. (London)*, 1980, 200.
2 E. S. Raper, *Coord. Chem. Rev.*, 1985, **61**, 115.
3 P. Mura, B. G. Olby, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1985, 2101.
4 M. Masaki, S. Matsunami, and H. Ueda, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3298.
5 F. P. Mullins, *J. Inorg. Nucl. Chem.*, 1979, **41**, 463.
6 A. J. Crowe and P. J. Smith, *J. Organomet. Chem.*, 1982, **224**, 223.
7 B. P. Kennedy and A. B. P. Lever, *Can. J. Chem.*, 1972, **50**, 3488.
8 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
9 J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, 1978, **24**, 251.
10 R. Graziani, U. Casellato, R. Ettorre, and G. Plazzogna, *J. Chem. Soc., Dalton Trans.*, 1982, 805.
11 R. Bardi, A. M. Piazzesi, R. Ettorre, and G. Plazzogna, *J. Organomet. Chem.*, 1984, **270**, 171.
12 G. Valle, G. Plazzogna, and R. Ettorre, *J. Chem. Soc., Dalton Trans.*, 1985, 1271.
13 B. R. Penfold, *Acta Crystallogr.*, 1953, **6**, 707.
14 E. Binamira-Soriaga, M. Lundeen, and K. Seff, *Acta Crystallogr., Sect. B*, 1979, **35**, 2875.
15 S. C. Kokkou, S. Fortier, P. J. Rentzeperis, and P. Karagiannidis, *Acta Crystallogr., Sect C*, 1983, **39**, 178.
16 N. Trinajstić, *Tetrahedron Lett.*, 1968, **12**, 1529.
17 F. A. K. Nasser, M. B. Hossain, D. van der Helm, and J. J. Zuckerman, *Inorg. Chem.*, 1984, **23**, 606.
18 G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960.
19 E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc. A*, 1969, 913.
20 D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. A*, 1967, 1759.
21 R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.
22 T. R. Spalding, *J. Organomet. Chem.*, 1973, **55**, C65.

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