Preparation, characterization and crystal structure of tetrakis[1-methyl-2(3*H*)-imidazolinethione] dimethyltin(IV) nitrate

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Abstract

The synthesis and characterization (IR, ^1H and ^{119}Sn NMR, and mass spectra) of $[SnMe_2(Hmimt)_4](NO_3)_2$ (Hmimt = 1-methyl-2(3*H*)-imidazolinethione) are described. The crystal structure has been determined by X-ray crystallography and refined to $R = 0.044$, using 2277 observed reflections. The compound is triclinic, space group $P\bar{1}$, with $a = 10.733(2)$, $b = 10.008(2)$, $c = 7.594(2)$ Å, $\alpha = 110.49(3)$, $\beta = 104.71(3)$ and $\gamma = 82.60(3)°$. The tin atom is octahedrally coordinated and lies on a crystallographic inversion centre. The Hmimt ligand, bound via the S atom (the mean of the two independent Sn–S distances is 2.735 Å), maintains its thione form in the complex. The nitrate ions are involved in hydrogen bonding with the NH groups of the ligands.

Introduction

The dimethyltin(IV) cation, $SnMe_2^{2+}$, was studied spectroscopically in aqueous solution by McGrady and Tobias [1, 2] who suggested the presence of a linear C–Sn–C skeleton and, probably, four equatorial water molecules coordinated to the cation by highly polar bonds. Although this complex could not be isolated, several cationic $SnMe_2^{2+}$ complexes with monodentate ligands have been prepared [3, 4] and characterized by IR and NMR spectroscopy.

As part of an extensive work on the interaction of dialkyltin(IV) compounds with sulfydrylated ligands [5, 6], we report here on the preparation and structural characterization of the complex $[SnMe_2(Hmimt)_4](NO_3)_2$ (Hmimt = 1-methyl-2(3*H*)-imidazolinethione). As far as we know this is the first cationic complex of $SnMe_2^{2+}$ with monodentate ligands studied by X-ray diffraction.

Experimental

Synthesis of $[SnMe_2(Hmimt)_4](NO_3)_2$

0.9516 g of $AgNO_3$ (5.6 mmol) in 20 ml of distilled water was added to 0.6153 g of $SnMe_2Cl_2$ (2.8 mmol), and the white solid formed after stirring was filtered off. The filtrate was slowly mixed, with stirring, with 1.2792 g of Hmimt (11.2 mmol) in 20 ml of distilled water. After three days of stirring, the water was evaporated off and the solid formed was recrystallized from acetone. *Anal.* Found: C, 29.5; N, 18.8; H, 4.2; S, 17.4. Calc. for $[SnMe_2(Hmimt)_4](NO_3)_2$: C, 29.6; N, 19.2; H, 4.1; S, 17.6%. m.p. = 138 °C. The mass spectrum showed peaks at *m*/*e* (ion, intensity): 69 (HIm + H, 26.2); 81 (HL − S − H, 23.0); 114 (HL, 100); 120 (Sn, 1.9); 135 (SnMe, 3.2): 212 ($SnMe_2NO_3$, 2.5); 233 (SnL, 11.4); 249 (SnMeHL, 7.8); 263 ($SnLMe_2$, 15.6); 295 ($SnLNO_3$, 2.6); 310 ($SnMeLNO_3$, 11.0). Crystals suitable for X-ray analysis were obtained from acetone solutions by slow evaporation of the solvent.

Measurements

Elemental analyses were performed with a Carlo-Erba 1108 apparatus. Melting point was measured in a Büchi apparatus. IR spectra were recorded in Nujol mulls or KBr discs on a Perkin-Elmer 180 spectrophotometer. Conductivity measurements were made on a WTW-LF3 conductivity meter. Mass spectra were recorded on a Kratos MS50 TC spectrometer connected to a DS90 system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C); ions were

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identified by DS90 software. NMR spectra were recorded on a Bruker WM-250 spectrometer. ^{1}H chemical shifts were referred to DSS (D_2O spectra) and TMS (DMSO and CD_2Cl_2 spectra) and the ^{119}Sn chemical shift (in CD_2Cl_2) to tetramethyltin.

Crystal structure determination

A crystal of maximum dimension 0.2 mm was selected and used for the X-ray analysis. Data were collected in a Philips PW 1100 diffractometer using Mo Kα radiation. The crystal was stable under irradiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. 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. Refinement of scale factor and positional and thermal parameters was performed minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift among the refined parameters of the non-hydrogen atoms was 0.2 times the standard deviation. No significant residual of electronic density was observed in the final electron density of electronic density map. Form factors for the atoms were supplied internally by the SHELX program system [7]. Crystal and intensity data, final atomic parameters and bond distances and angles are listed in Tables 1, 2 and 3, respectively.

TABLE 1. Crystal and intensity data for $[SnMe_2(Hmimt)_4](NO_3)_2$

Formula	$C_{18}H_{30}N_{10}O_6S_4Sn$
Formula weight	729
Cell constants	
a (Å)	10.733(2)
b (Å)	10.008(2)
c (Å)	7.594(2)
α (°)	110.49(3)
β (°)	104.71(3)
γ (°)	82.60(3)
V (Å^3)	738
Density (calc), D_c (g cm^{-3})	1.64
Molecules per cell, *Z*	1
System	triclinic
Space group	$P\bar{1}$
Absorption (Mo Kα) (cm^{-1})	$\mu = 18.6$
Wave length (Mo Kα) (Å)	$\lambda = 0.7107$
Scan method	$\theta/2\theta$
2θ limits (°)	$2 < 2\theta < 50$
Scan speed (°/min)	2
Data collected	2796
Data with $I > 3\sigma(I)$	2277
Corrections applied	Lp, absorption [8]
Discrepancy factor, *R*	0.044

TABLE 2. Fractional coordinates with equivalent isotropic thermal parameters (×100)

Atom	*x*	*y*	*z*	U_{eq}[a]
Sn(1)	0.0	0.0	0.0	3.91(3)
S(1)	−0.1778(1)	−0.0338(2)	−0.3412(2)	5.04(8)
S(2)	0.0200(2)	−0.2900(2)	−0.0915(2)	5.00(8)
N(1)	−0.3991(5)	0.0957(5)	−0.2274(6)	4.4(2)
N(2)	−0.4020(5)	−0.1340(5)	−0.3389(7)	5.2(3)
N(3)	−0.0860(5)	−0.3301(5)	0.1795(6)	4.4(3)
N(4)	−0.2134(5)	−0.3732(5)	−0.0995(7)	5.1(3)
C(1)	−0.3273(5)	−0.0223(6)	−0.2984(7)	4.2(3)
C(2)	−0.3596(7)	0.2424(6)	−0.1680(11)	6.4(4)
C(3)	−0.5177(6)	0.0587(7)	−0.2235(9)	5.7(4)
C(4)	−0.5199(6)	−0.0839(7)	−0.2926(9)	6.0(4)
C(5)	−0.0951(5)	−0.3309(5)	−0.0004(8)	4.2(3)
C(6)	0.0295(6)	−0.2985(7)	0.3356(9)	5.8(3)
C(7)	−0.1990(6)	−0.3680(6)	0.1951(10)	5.5(4)
C(8)	−0.2792(6)	−0.3973(6)	0.0195(10)	5.9(4)
C(9)	0.1462(5)	−0.0243(6)	−0.1574(8)	4.4(3)
N(5)	0.3634(5)	0.5309(5)	0.5957(7)	5.1(3)
O(1)	0.3157(5)	0.4149(5)	0.4849(7)	7.6(3)
O(2)	0.3201(8)	0.6356(7)	0.5531(13)	14.8(6)
O(3)	0.4393(7)	0.5387(9)	0.7392(9)	12.7(5)
H(21)	−0.434	0.315	−0.110	
H(22)	−0.336	0.274	−0.279	
H(23)	−0.275	0.244	−0.056	
H(3)	−0.594	0.131	−0.174	
H(4)	−0.598	−0.148	−0.311	
H(61)	0.000	−0.311	0.455	
H(62)	0.060	−0.191	0.376	
H(63)	0.109	−0.374	0.302	
H(7)	−0.220	−0.375	0.323	
H(8)	−0.377	−0.432	−0.019	

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

Mass spectra

The presence in the spectra of a very intense [HL] ion signal and several others due to its fragmentation, and the absence of any signal due to the 'molecular' ion, are in keeping with the fast fragmentation of the tin compound under EI conditions following a pathway in which the breaking of the Sn–S bond is an essential step.

X-ray structure

The crystal structure of the ionic complex is shown in Fig. 1 together with the numbering scheme used. As the metal atom lies on the (crystallographic) inversion centre of the *trans*-octahedral complex cation, the asymmetric unit of the structure comprises one half of the complex, which affords the opportunity to compare the structural details of two Hmimt ligands that are not interchanged by the inversion operation. As shown in the Figure, the four Hmimt ligands are arranged in a rather symmetrical way, so that, apart from the crys-

TABLE 3. Selected bond distances (Å) and angles (°)

Sn(1)–S(1)	2.741(1)	Sn(1)–S(2)	2.730(1)
Sn(1)–C(9)	2.145(5)	S(1)–C(1)	1.698(6)
S(2)–C(5)	1.713(6)	N(1)–C(1)	1.346(7)
N(1)–C(2)	1.466(7)	N(1)–C(3)	1.361(7)
N(2)–C(1)	1.361(7)	N(2)–C(4)	1.384(8)
N(3)–C(5)	1.342(7)	N(3)–C(6)	1.461(7)
N(3)–C(7)	1.360(7)	N(4)–C(5)	1.337(7)
N(4)–C(8)	1.377(8)	C(3)–C(4)	1.338(9)
C(7)–C(8)	1.347(9)	N(5)–O(1)	1.252(6)
N(5)–O(2)	1.206(8)	N(5)–O(3)	1.168(7)
N(2)...O(1$^{\mathrm{I}}$)	2.768(8)	N(4)...O(1$^{\mathrm{I}}$)	2.752(8)
S(2)–Sn(1)–C(9)	86.6(2)	S(1)–Sn(1)–C(9)	87.4(2)
S(1)–Sn(1)–S(2)	88.7(0)	Sn(1)–S(1)–C(1)	108.4(2)
Sn(1)–S(2)–C(5)	105.4(2)	C(2)–N(1)–C(3)	124.5(5)
C(1)–N(1)–C(3)	110.1(5)	C(1)–N(1)–C(2)	125.3(5)
C(1)–N(2)–C(4)	109.9(5)	C(6)–N(3)–C(7)	124.3(5)
C(5)–N(3)–C(7)	110.3(5)	C(5)–N(3)–C(6)	125.3(5)
C(5)–N(4)–C(8)	109.8(5)	N(1)–C(1)–N(2)	105.6(5)
S(1)–C(1)–N(2)	126.0(4)	S(1)–C(1)–N(1)	128.4(4)
N(1)–C(3)–C(4)	107.5(6)	N(2)–C(4)–C(3)	106.9(5)
N(3)–C(5)–N(4)	106.1(5)	S(2)–C(5)–N(4)	125.7(4)
S(2)–C(5)–N(3)	128.2(4)	N(3)–C(7)–C(8)	107.0(6)
N(4)–C(8)–C(7)	106.7(5)	O(2)–N(5)–O(3)	121.6(7)
O(1)–N(5)–O(3)	121.8(7)	O(1)–N(5)–O(2)	116.4(6)

Symmetry codes: none $=x, y, z$; $^{\mathrm{I}}=1-x, 1-y, 1-z$.

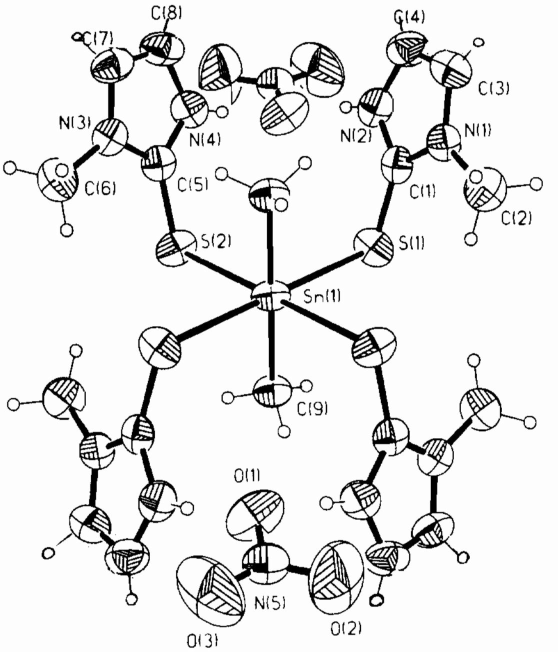


Fig. 1. The crystal structure of [SnMe$_2$(Hmimt)$_4$](NO$_3$)$_2$.

tallographic inversion centre at the metal position, the C_{2h} local symmetry can be roughly attributed to the complex cation, with the two-fold axis bisecting the S(1)–Sn–S(2$^{\mathrm{I}}$) angle in the plane perpendicular to C(9)–C(9$^{\mathrm{I}}$) and the mirror plane passing through Sn perpendicular to the two-fold axis.

The Sn–S bond distance (mean 2.735 Å), agrees well with those found in SnCl$_2$Me$_2$(pyrt)$_2$, 2.729(2) Å [9], and SnCl$_2$(CH=CH$_2$)(imt)$_2$, 2.733(1) Å [10], and is close to the average of the Sn–S distances found in several Me$_2$Sn(chelate)$_2$ systems prepared with S-donor ligands (ref. 11 and refs. therein). The Sn–C distance is slightly longer than in these chelate complexes.

The thione form possessed by the free Hmimt molecule [12] is maintained in the coordinated ligand, the labile hydrogens being attached to N(2) and N(4). The double bond character is well localized in the inter-C bond (mean 1.342(9) Å), and the C–N distances involving the thioamide carbons C(1) and C(5) are shorter (mean of four values 1.346 Å), than the others (mean 1.370 Å), the exocyclic C−N bonds being the longest (1.464(7) Å). As previously observed in some complexes with this or parent molecules [5, 6, 9, 12, 13], the π character of the C=S bond is reduced upon coordination, the C=S distance being longer than in the free ligand (mean 1.706(6) Å in this complex, 1.685(2) Å in Hmimt).

The bond angles in the coordinated ligands are also similar to those reported for the free molecule, with the largest internal angles at the nitrogen atoms. One minor difference lies in the observed asymmetry of the external S−C−N angles, those involving the methylated nitrogen being systematically wider than those involving NH (128.3(4)° as against 125.8(5)°), whereas they are equal in free Hmimt.

Atom O(1) of each nitrate ion is involved in two hydrogen bonds with the NH groups of the adjacent mimt ligands (see Table 3). The planar nitrate ions, which have their normal bond distances and angles [14], bridge two arms of the same cation, and in this way form part of the complex molecule. Similar hydrogen bonds with nitrate [14], perchlorate [15] and chloride [16–18] ions have been found in other complexes of this ligand with divalent cations, though in different structural environments.

TABLE 4. Significant IR bands of Hmimt and [SnMe$_2$(Hmimt)$_4$](NO$_3$)$_2$

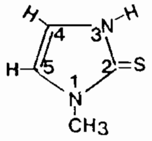
[SnMe$_2$(Hmimt)$_4$](NO$_3$)$_2$	Hmimt	Assignment
3140, 3120(s)$^{\mathrm{a}}$	3120(s)	ν(N−H)
1575(s)	1570(s)	ν(C=C) + ν(C=N)
1465(s,b)	1460(s,b)	thioamide I
1280(s)	1280(s)	thioamide II
1100(m), 1090(m)	1090(s)	thioamide III
750(m)	770(sh) 740(m)	thioamide IV
680(s)	675(s)	δ(C=S)
510(m)	530(s)	π(C=S)

$^{\mathrm{a}}$s = strong; b = broad; m = medium; sh = shoulder.

TABLE 5. ^{1}H NMR parameters (δ in ppm, J in Hz)

Compound	Solvent	δ(H-N)	δ(H-5)	δ(H-4)	δ($N-CH_3$)	δ($Sn-CH_3$)	$^2J(^{119/117}Sn-^1H)$
Hmimt	D_2O		7.00(d)^a	6.93(d)	3.55(s)		
$[SnMe_2(Hmimt)_4](NO_3)_2$	D_2O		7.02(d)	6.94(d)	3.57(s)	0.97(s)	107.0/102.8
Hmimt	DMSO	12.03(s,b)	7.03(d)	6.85(d)	3.40(s)		
$[SnMe_2(Hmimt)_4](NO_3)_2$	DMSO	12.00(s,b)	7.03(d)	6.84(d)	3.41(s)	0.90(s)	111.7/107.3
Hmimt	CD_2Cl_2	11.50(s,b)	6.69(d)		3.53(s)		
$[SnMe_2(Hmimt)_4](NO_3)_2$	CD_2Cl_2		6.89(d)	6.82(d)	3.61(s)	1.12(s)	87.8/84.0

^{a}s = singlet, d = doublet, b = broad.
Numbering scheme:



IR spectra

Table 4 lists the significant bands of the free [13] and complexed ligand. The shifts that these bands undergo upon complexation are very slight and similar to those found in other S-coordinated complexes of this ligand (ref. 13 and refs. therein). ν_{asym} (C–Sn–C) reinforces a ligand band at 610 cm^{-1}, and a medium band at 290 cm^{-1} is tentatively attributed to ν(Sn–S). The compound also shows bands at 1340, 1020 and 830 cm^{-1} that are characteristic of the nitrate ion [19].

Characteristics in solution

Conductivity

The molar conductivities in water, dimethyl sulfoxide and acetonitrile (550.4, 95.1 and 22.3 Ω^{-1} cm^2 mol^{-1}, respectively) reflect different behaviours of the $[SnMe_2(Hmimt)_4](NO_3)_2$ complex. Whereas in water and DMSO the compound behaves as a 2:1 electrolyte [20, 21] (the high value in water may be due to interchange of ligand and water and partial hydrolysis of the $SnMe_2{}^{2+}{}_{(aq)}$ cation [20]), the conductivity in acetonitrile is typical of a non-electrolyte. A similar non-electrolytic behaviour has previously been reported for the ionic compounds $Pt(Hmimt)_4Cl_2$, $M(Hmimt)_4(NO_3)_2 \cdot H_2O$ (M=Co, Zn) and $Cd(Hmimt)_4(NO_3)_2$ [18, 19] in nitromethane, a solvent with a dielectric constant similar to that of acetonitrile, and was attributed to the interchange that can take place between the ligands of the coordination sphere and the X$^-$ ions (Cl$^-$, $NO_3{}^-$).

NMR studies

Table 5 lists NMR data for Hmimt and the complex in D_2O, DMSO and CD_2Cl_2, with Hmimt signals assigned following Buncel *et al.* [22]. The ligand signals for solutions of free Hmimt and the complex in D_2O and DMSO are almost identical suggesting that in this medium Hmimt is displaced from the complex by the solvent; the values of $^2J(^{119/117}Sn-^1H)$ for the compound in D_2O are practically identical to those obtained by McGrady and Tobias [1] for a 2 M solution of $SnMe_2(ClO_4)_2$ in water.

The situation is different in CD_2Cl_2. The ^{1}H NMR spectra of the complex show the ligand signals shifted to lower field as the result of coordination. The $^2J(^{119/117}Sn-^1H)$ values suggest [23] that the six-coordination observed in the solid state persists in CD_2Cl_2 solution. The insensitivity of this parameter to addition of a large excess of Hmimt to the solution supports this hypothesis, and seems to rule out any significant dissociation of the ligand when the complex is dissolved in this medium.

Although the ^{119}Sn chemical shift must be interpreted cautiously when hexacoordinated dimethyltin(IV) compounds are concerned [24], the value observed for this cationic Hmimt complex (−174.2 ppm in CD_2Cl_2 solution) lies inside the range proposed [25] for derivatives with this coordination number.

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