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Cationic complexes of diorganotin(IV) derivatives. The crystal structure of tetrakis[1-methyl-2(3H)-imidazolinethione]diethyltin(IV) nitrate

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Abstract

$[SnEt_2(Hmimt)_4](NO_3)_2$ (Hmimt = 1-methyl-2(3*H*)-imidazolinethione) has been synthesized and characterized by mass spectrometry, IR, Raman, Mössbauer, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, and its crystal structure determined by X-ray crystallography. The coordination distances in the centrosymmetric octahedral cation are 2.163(5) Å for Sn–C, and 2.729(2) and 2.752(2) Å for Sn–S, and the $[SnEt_2(Hmimt)_4](NO_3)_2$ units are interconnected by hydrogen bonds via their nitrate ions.

Keywords: Tin; X-ray structure; Diethyltin complex

1. Introduction

Although several cationic complexes of the type $[SnMe_2L_4]^{2+}$ with unidentate ligands L have been prepared and characterized by IR and NMR spectroscopy [1], it is only very recently that the structures of the typical examples $[SnMe_2(H_2O)_4]^{2+}$ [2], $[SnMe_2(OSMe_2)_4]^{2+}$ [3] and $[SnMe_2(Hmimt)_4]^{2+}$ (Hmimt = 1-methyl-2(3*H*)-imidazolinethione) [4] have been elucidated by X-ray crystallography. In $[SnMe_2(Hmimt)_4]^{2+}$ the four Hmimt ligands are located equatorially in a distorted octahedral structure, forming a planar SnS_4 nucleus reminiscent of $[M(Hmimt)_4]^{2+}$ (M = Pt or Pd) [5,6] except that the Hmimt ligands have different orientations due to the steric influence of the two methyl groups. To investigate the influence of more bulky R groups on both Hmimt orientation and overall structure, we have now prepared the similar complex $[SnEt_2(Hmimt)_4]^{2+}$ as its nitrate, tetrakis [1-methyl-2(3*H*)-imidazolinethione]diethyltin(IV) nitrate, the crystal structure and spectroscopic properties of which we describe in this paper. As far as we know, this is the first cationic diethyltin complex of the form $[SnEt_2L_4]^{2+}$ to have been studied crystallographically.

2. Experimental details

2.1. Synthesis of $[SnEt_2(Hmimt)_4](NO_3)_2$

$AgNO_3$ (0.574 g, 3.4 mmol) in 15 ml of distilled water was added to 0.419 g of $SnEt_2Cl_2$ (1.7 mmol) and the white solid formed after stirring filtered off. The filtrate was added slowly, with stirring, to 0.772 g of Hmimt (6.8 mmol) in 15 ml of distilled water. After stirring for 3d, 10 ml of acetone was added and the solution slowly concentrated to yield crystals suitable for X-ray analysis. Analysis Found: C, 31.7; N, 18.5; H, 4.5%. Calc. for $[SnEt_2(Hmimt)_4](NO_3)_2$: C, 31.7; N, 18.5; H, 4.5%. M.p. 110°C.

2.2. Measurements

Elemental analysis was performed with a Carlo-Erba 1108 apparatus. The melting point of $[SnEt_2(Hmimt)_4](NO_3)_2$ was measured with a Büchi apparatus. IR spectra were recorded in Nujol mulls or KBr discs on a Perkin-Elmer 180 spectrophotometer, and Raman

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spectra with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å). Conductivity measurements were made using a WTW-LF3 conductivity meter. Mössbauer spectra were recorded on a Laben Master 4000 instrument at 80 K using a Harwell cryostat. The $Ca^{119}SnO_3$ source (15 mCi, New England Nuclear) was moved at room temperature and constant acceleration with a triangular wave form. Computer programs were employed to fit Lorentzian line shapes to the experimental spectra. Isomer shifts, δ, are relative to SnO_2. NMR spectra were recorded on a Bruker WM-250 spectrometer. ^1H (250.13 MHz) and ^{13}C (62.86 MHz) chemical shifts (in CD_2Cl_2) were referred to TMS via the solvent peak, and ^{119}Sn (93.28 MHz) chemical shifts to tetramethyltin.

2.3. *Crystal structure determination*

A crystal of maximum dimension 0.2 mm was used. Intensity data were obtained using Mo Kα radiation on a Philips PW 1100 diffractometer. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table 1. The compound was stable under irradiation. The structure was solved by standard methods, followed by full-matrix least-squares refinement of the atomic parameters. H atoms were located on the electron density maps, except those of the Me and Et groups, which were introduced in calculated positions with fixed C–H distances and isotropic temperature factors (C–H = 1.08 Å, U_{iso} = 0.08 Å^2). Anisotropy was introduced for non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters was achieved by minimizing the function $\Sigma w(\Delta F)^2$ with w = 1. Form factors for the atoms were supplied internally by the SHELX program system [8]. Final atomic parameters are listed in Table 2. Bond distances and angles are reported in Table 3. Structural data have been deposited at the Cambridge Crystallographic Data Center.

Table 1
Crystal and intensity data

Formula	$C_{20}H_{34}N_{10}O_6S_4Sn$
Formula weight	757.5
a (Å)	8.984(3)
b (Å)	9.638(4)
c (Å)	10.852(4)
α (°)	79.60(2)
β (°)	112.60(3)
γ (°)	113.73(2)
V (Å^3)	793.8(6)
D_c (g cm^{-3})	1.58
Molecules per cell, *Z*	1
System	Triclinic
Space group	$P\bar{1}$
F(000)	386
Absorption (Mo Kα)(cm^{-1}), μ	10.2
Wavelength (Mo Kα) (Å)	0.7107
Scan method	$\theta/2\theta$
2θ limits (°)	$4 < 2\theta < 50$
Scan speed (deg min^{-1})	2
Unique reflections	3117
Observed intensities	2773
Corrections applied	Lp, absorption [7]
Discrepancy factor, *R*	0.032
Greatest shift (e.s.d.)	0.6
Greatest map residual (e Å^{-3})	1.4

Table 2
Fractional coordinates with equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	U_{eq} (Å^2)
Sn(1)	0.0	0.0	0.0	0.0323(1)
S(1)	−0.3168(1)	−0.08898(1)	−0.19756(9)	0.0429(4)
S(2)	−0.0364(1)	0.2726(1)	−0.0109(1)	0.0488(5)
N(1)	−0.2176(5)	−0.0197(4)	−0.4157(3)	0.047(2)
N(2)	−0.3078(4)	0.1436(4)	−0.3853(3)	0.042(1)
C(1)	−0.2801(5)	0.0122(4)	−0.3367(4)	0.038(2)
C(2)	−0.2029(7)	0.0906(6)	−0.5154(4)	0.059(2)
C(3)	−0.2596(7)	0.1892(5)	−0.4972(4)	0.056(2)
C(4)	−0.3805(6)	0.2182(5)	−0.3318(5)	0.057(2)
N(3)	0.2845(5)	0.4497(4)	0.1476(3)	0.045(2)
N(4)	0.2336(4)	0.5105(4)	−0.0604(3)	0.042(1)
C(5)	0.1654(5)	0.4119(4)	0.0265(4)	0.037(2)
C(6)	0.4274(6)	0.5729(5)	0.1381(5)	0.052(2)
C(7)	0.3947(6)	0.6098(5)	0.0093(5)	0.052(2)
C(8)	0.1466(7)	0.5149(6)	−0.2053(4)	0.064(2)
C(9)	0.1507(5)	0.1029(5)	−0.1297(4)	0.043(2)
C(10)	0.2528(7)	0.0191(5)	−0.1423(5)	0.067(3)
O(1)	0.7686(5)	0.7416(4)	0.4125(3)	0.069(2)
O(2)	0.7407(10)	0.5261(5)	0.4916(6)	0.224(8)
O(3)	0.8216(5)	0.7008(4)	0.6229(3)	0.074(2)
N(5)	0.7753(6)	0.6540(4)	0.5082(4)	0.065(2)

3. Results and discussion

3.1. *X-Ray structure*

The crystal structure of $[SnEt_2(Hmimt)_4](NO_3)_2$ is shown in Fig. 1 together with the numbering scheme used. The crystal consists of $[SnEt_2(Hmimt)_4]^{2+}$ cations and nitrate anions. In the cation, the tin atom is coordinated to two ethyl groups and four Hmimt in a distorted octahedral structure with no symmetry apart from the crystallographic centre of inversion. In the coordination polyhedron, the Sn–C bond lengths are similar to those found in other octahedral organotin(IV) compounds and the two Sn–S bond lengths, although slightly different, have a mean value of 2.740 Å, similar to the mean of 2.735 Å found previously in $[SnMe_2(Hmimt)_4](NO_3)_2$ [4]. Distortions in coordination angles relative to a truly octahedral structure appear to be caused mainly by the asymmetry of the Hmimt, the greatest distortion occurring in the S(1)–Sn–C(9) angle, found to be 96.6°. The S(1)–Sn–S(2) angle is 86.3°,

Table 3
Bond distances (Å) and angles (°)

Sn–S(1)	2.729(2)	Sn–S(2)	2.752(2)
S(1)–C(1)	1.715(4)	S(2)–C(5)	1.710(3)
C(1)–N(1)	1.322(7)	C(5)–N(3)	1.335(5)
C(1)–N(2)	1.363(6)	C(5)–N(4)	1.349(5)
N(1)–C(2)	1.378(6)	N(3)–C(6)	1.378(5)
C(2)–C(3)	1.32(1)	C(6)–C(7)	1.325(7)
C(3)–N(2)	1.384(7)	C(7)–N(4)	1.374(5)
N(2)–C(4)	1.449(8)	N(4)–C(8)	1.463(5)
Sn–C(9)	2.163(5)	N(5)–O(1)	1.213(5)
C(9)–C(10)	1.50(1)	N(5)–O(2)	1.173(8)
		N(5)–O(3)	1.257(6)
S(1)–Sn–S(2)	86.88(6)	S(1)–Sn–C(9)	96.6(1)
Sn–C(9)–C(10)	116.7(3)	S(2)–Sn–C(9)	87.8(1)
Sn–S(1)–C(1)	104.4(2)	Sn–S(2)–C(5)	107.9(4)
S(1)–C(1)–N(1)	126.9(3)	S(2)–C(5)–N(3)	127.2(3)
S(1)–C(1)–N(2)	126.0(3)	S(2)–C(5)–N(4)	126.8(3)
C(1)–N(1)–C(2)	109.9(4)	C(5)–N(3)–C(6)	110.4(4)
C(1)–N(2)–C(3)	107.4(4)	C(5)–N(4)–C(7)	109.1(4)
C(1)–N(2)–C(4)	126.0(4)	C(5)–N(4)–C(8)	125.3(4)
N(1)–C(2)–C(3)	107.0(4)	N(3)–C(6)–C(7)	106.5(4)
C(2)–C(3)–N(2)	108.6(4)	C(6)–C(7)–N(4)	108.1(4)
C(3)–N(2)–C(4)	126.5(4)	C(7)–N(4)–C(8)	125.5(4)
O(1)–N(5)–O(2)	118.7(6)	O(1)–N(1)–O(3)	120.2(4)
O(2)–N(5)–O(3)	121.1(5)		
Hydrogen bonds [a]			
N(1) ··· O(1^{I})	3.150(7)	NH ··· O	2.47(7)
N(1) ··· O(3^{I})	2.793(6)	NH ··· O	1.89(6)
N(3) ··· O(3^{II})	2.937(6)	NH ··· O	2.06(6)

[a] Symmetry codes: none = x, y, z; I = $x-1, y-1, z-1$; II = $-x+1, -y+1, -z+1$.

while the torsional angles S(1)–Sn–C(9)–C(10) and S(2)–Sn–C(9)–C(10) describing the orientation of the ethyl groups relative to the Sn–S bonds are 72.8° and 13.8°, respectively, so that the terminal C(10) atom lies only 0.32 Å out of the plane defined by S(2), Sn and C(9). The two co-ordinated non-equivalent forms of the Hmimt both have geometries very similar to those found previously [4 and references therein], with the double bonds well localized at C(2)–C(3) and C(6)–C(7) and with C–S bond lengths which, although ca. 0.03 Å longer than in the unbound Hmimt [9] due to the reduction of π-character upon coordination, nevertheless indicate that the thione form basically remains in the complex. Some of the distances between ring N–H groups and the nitrate ions of neighbouring $[SnEt_2(Hmimt)_4](NO_3)_2$ units (Table 3) strongly suggest the presence of interconnecting hydrogen bonds stabilizing the crystal structure.

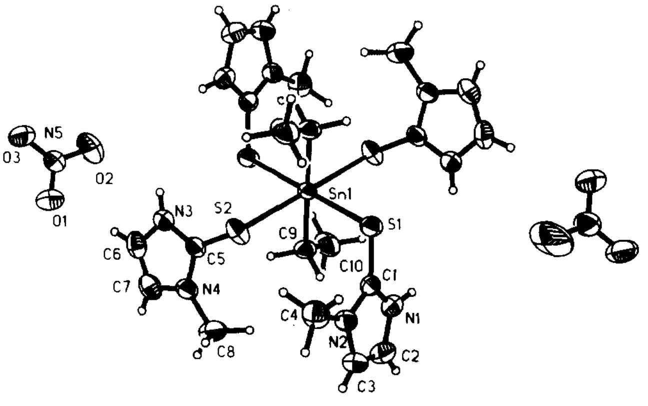


Fig. 1. Perspective view of $[SnEt_2(Hmimt)_4](NO_3)_2$ showing the atom numbering scheme.

Although $[SnMe_2(Hmimt)_4](NO_3)_2$ [4] also has an SnC_2S_4 nucleus and N–H groups involved in hydrogen bonds, several structural differences between the methyl and ethyl compounds deserve further comment. In particular, whereas the Sn–C and Sn–S bond distances in $[SnR_2(Hmimt)_4](NO_3)_2$ are affected very little by whether R is Me or Et (the distortion in the coordination polyhedron is just slightly greater when R is Et), the two structures differ significantly as regards both their hydrogen bonding and the mutual orientation of the imidazoline rings. In the methyl derivative, a single O atom of a nitrate ion is involved in two equivalent hydrogen bonds with the N–H groups of the adjacent Hmimt of its own unit in a structure with a twofold axis bisecting the S(1)–Sn–S(2) angle. In the ethyl derivative the hydrogen bonds in which N(1) and N(3) are involved are nonequivalent and a second O atom of the nitrate ion is involved in another, albeit weaker, hydrogen bond. (Table 3). These differences, together with the difference in bulkiness between the methyl and ethyl groups, probably explain the different Hmimt orientations in the two structures.

3.2. *Vibrational spectra*

The shifts that the significant IR and Raman Hmimt bands [10] undergo upon complexation are similar to those observed for the methyl derivative and other tin complexes of this ligand [4,11]. The organometallic fragment of the compound gives rise to bands at 510 cm^{-1} [IR, ν_{asym}(Sn–C)] and 461 cm^{-1} [R, ν_{sym}(Sn–C)].

3.3. *Mössbauer spectra*

The Mössbauer parameters (δ, 1.81 mm s^{-1}; ΔE_Q, 3.50 mm s^{-1}) are consistent with the *trans*-octahedral coordination geometry around the tin shown by the X-ray analysis, even though the quadrupole splittings are lower than expected for compounds with a C–Sn–C bond angle of 180° which normally have $\Delta E_Q > 4.0$ mm s^{-1}. This means that the very large EFG contribution of the two apical alkyl groups must be counterbalanced in some way by the four equatorial ligands. This kind of compensation is usual in complexes with S-donors for which large negative p.q.s. have been calculated [12], and Hmimt is not an exception. In a previous

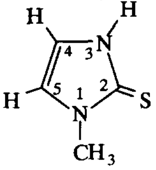
Table 4
^{1}H, ^{13}C and ^{119}Sn NMR parameters [chemical shifts (δ) in ppm referred to TMS (^{1}H, ^{13}C) or $SnMe_4$ (^{119}Sn); J in Hz; solvent CD_2Cl_2]

Compound	CH_3—	—CH_2—	$^2J(^{119}Sn-^1H)$	$^3J(^{119}Sn-^1H)$	CH_3–N	H(4)	H(5)	N–H
Hmimt	–	–	–	–	3.53 (s) [a]	6.69 (d)		11.50 (s,b)
$SnEt_2(NO_3)_2$	1.44 (t)	2.06 (q)	59.1	153.2	–	–	–	–
$[SnEt_2(Hmimt)_4](NO_3)_2$	1.25 (t)	1.82 (q)	77.2	164.5	3.59 (s)	6.81 (d)	6.87 (d)	10.36 (s,b)

Compound	CH_3—	—CH_2—	$J(^{119}Sn-^{13}C)$	$^2J(^{119}Sn-^{13}C)$	CH_3–N	C(4)	C(5)	C(2)	^{119}Sn
Hmimt	–	–	–	–	34.4	114.2	119.5	161.2	–
$SnEt_2(NO_3)_2$	9.1	21.1	521.2	47.7	–	–	–	–	−213.5
$[SnEt_2(Hmimt)_4](NO_3)_2$	10.1	24.7	–	49.4	34.8	115.9	120.5	157.0	−167.8

[a] s = singlet, d = doublet, t = triplet, q = quartet, b = broad

Numbering scheme:



paper, we suggested [13] a p.q.s. of −0.36 mm s^{-1} for Hmimt on the basis of structural data for $[SnPh_2Cl_2(Hmimt)_2]$. Correlation of the ΔE_Q values and bond angles now available for a wider range of compounds [4,11,14] yields a value of −0.18 mm s^{-1} ($r = 0.91$). Unlike ΔE_Q, the value of the isomer shift of $[SnEt_2(Hmimt)_4](NO_3)_2$ is very high, especially if compared with that of the analogous methyl derivative (δ, 1.57 mm s^{-1}; ΔE_Q, 3.28 mm s^{-1}). However, the difference between these two isomer shifts is in keeping with those found for compounds of the type $[SnR_2X_2(Hmimt)_2]$ (R = Me or Et; X = Cl or Br) [11,14].

3.4. Characteristics in solution

3.4.1. Conductivity

The molar conductivity of $[SnEt_2(Hmimt)_4](NO_3)_2$ in dimethyl sulphoxide (92.6 S cm^2 mol^{-1}) differs greatly from its conductivity in acetonitrile (15.0 S cm^2 mol^{-1}). Whereas in DMSO this compound behaves as a 2:1 electrolyte [15], the conductivity in acetonitrile is typical of non-electrolytes. A similar behaviour was found for the methyl derivative [4] and was attributed to partial replacement of the Hmimt of the coordination sphere by the NO_3^- anions in acetonitrile.

3.4.2. NMR studies

Table 4 lists multinuclear magnetic resonance parameters for Hmimt, the complex and $SnEt_2(NO_3)_2$, the latter being included for comparative purposes. The ^{1}H NMR data for the Hmimt in the complex are very similar to those found in $[SnMe_2(Hmimt)_4](NO_3)_2$ [4] in the same solvent, the main difference being the presence of the N–H group signal which was not observed in the spectrum of the methyl compound. The shift of all the Hmimt signals except NH to higher frequencies upon complexation suggests that Hmimt remains coordinated in CD_2Cl_2 solution. In the ^{13}C NMR spectrum of the complex, CH_3–N, C(4) and C(5) also appear deshielded relative to the free base, but C(2) shifts toward lower frequencies possibly because the slight thione-to-thiol change of Hmimt upon complexation (vide supra) weakens the less shielding carbon–sulphur double bond and reinforces the more shielding carbon–nitrogen bond [16].

The spectroscopic behaviour of the organometallic moiety of the complex also shows the persistence of $SnEt_2$–Hmimt coordination in CD_2Cl_2 solution. All the ^{1}H and ^{13}C NMR parameters of $SnEt_2$ in $[SnEt_2(Hmimt)_4](NO_3)_2$ clearly differ from those of diethyltin(IV) nitrate (see Table 4), the complex having more shielded protons, less shielded carbons and bigger ^nJ(Sn–H) coupling constants. The ^{119}Sn chemical shifts also differ. In the Hmimt derivative the nuclide resonates at higher frequencies than in $SnEt_2(NO_3)_2$, possibly due to the sulphur atoms of the complex affording greater shielding than to the oxygen atoms of $SnEt_2(NO_3)_2$.

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