Notes

A Novel Pentameric Hydrolysis Product of $SnMe_2Cl_2$: Crystal and Molecular Structure of $[NHEt_3][(SnMe_2Cl)_5O_3]$ †

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The fortuitous isolation of $[NHEt_3][(SnMe_2Cl)_5O_3]$ (**1**) as a product of the partial hydrolysis of $SnMe_2Cl_2$ is described. The composition and structure of (**1**) have been resolved by *X*-ray crystallography {orthorhombic, space group *C2ca*, 2 173 observed reflections [$I/\sigma(I) > 3.0$], collected by a four-circle diffractometer, $R = 0.038$}. The anion is related to previous 'ladder' structures, and has trigonal-bipyramidal geometry for the tin atoms [Sn–O 2.140(10) (mean), Sn–C 2.123(10) Å (mean), Sn–Cl 2.459(4)—2.820(4) Å with longer interactions 3.186(4)—3.575(4) Å].

As part of a study of the toluene-3,4-dithiol (H_2tdt)–MR_xX_{4-x} system[1] (M = Si, Ge, or Sn; R = alkyl; X = halogen; $x = 1$—3) the reaction of $SnMe_2Cl_2$ with H_2tdt was investigated in the presence of triethylamine as a convenient abstractor for the expected release of HCl. Rather than *S,S'*-bidentate chelate formation of $SnMe_2(tdt)$, we obtained colourless crystals of the title compound $[NHEt_3][(SnMe_2Cl)_5O_3]$ (**1**) whose identity has been established by a single-crystal *X*-ray structural determination.

Experimental

Solvents were rigorously dried and distilled over CaH_2 and degassed by applying a positive pressure of N_2. Dichlorodimethyltin and toluene-3,4-dithiol (H_2tdt) were used as obtained commercially.

A solution of H_2tdt (1.63 g, 10.5 mmol) dissolved in benzene (10 cm^3) was added dropwise to a stirred solution of $SnMe_2Cl_2$ (2.28 g, 10.4 mmol) in benzene (50 cm^3), maintained at 0 °C under an atmosphere of nitrogen. NEt_3 (2.08 g, 20.5 mmol) in benzene (10 cm^3) was then added with gentle stirring, until the solution cleared to reveal a white precipitate separated from a red solution.

The reaction mixture was heated at reflux, under N_2 for 8 h after which the precipitate was removed. The filtrate was heated at reflux for a further 4 h and filtered again. The combined $[NHEt_3]Cl$ precipitates weighed 1.95 g when dry. Evaporation of the solvent from the resulting filtrate produced a small amount of an off-white solid soluble in benzene, dimethyl sulphoxide, and *NN*-dimethylformamide. This was recrystallised from benzene as colourless crystals of (**1**).

The identification of (**1**) as an oxo-bridged tin compound raises the question of the source of oxygen atoms. With no possibility of oxygen extraction from solvents/reagents, traces of water must have been present (despite rigorous drying of materials and continuous handling under a nitrogen atmosphere) and the formation of (**1**) can be viewed as resulting from the partial hydrolysis of $SnMe_2Cl_2$. Subsequent repetition of the preparation did not yield this hydrolysis product. Attempts to synthesise (**1**) by introducing controlled amounts of water into the reaction mixture were equally unsuccessful.

A direct synthesis according to equation (1) was also

$$5SnMe_2Cl_2 + 6NEt_3 + 3H_2O \longrightarrow [NHEt_3][SnMe_2Cl)_5O_3] + 5[NHEt_3]Cl \quad (1)$$

unsuccessful, although similar reactions have been used to prepare other $SnMe_2X_2$ (X = halogen) hydrolysis products.[2]

A mixture of $SnMe_2Cl_2$ (3.5 g, 16 mmol) and NEt_3 (0.5 cm^3) to which water (0.18 cm^3) had been introduced was dissolved in dry degassed benzene (50 cm^3). The resulting mixture was left stirring for 36 h when the white precipitate was removed, leaving a colourless solution. Work-up of this failed to produce the desired product.

Although we have been unable to establish a repeatable synthetic route to (**1**), it has been completely characterised by *X*-ray structural analysis; no chemical analysis is available because of the low yield in the original reaction. No further investigation of this system is planned.

Crystal Data.—Colourless, block-like crystals, $[C_6H_{16}N]$-$[C_{10}H_{30}Cl_5O_3Sn_5]$, orthorhombic, space group *C2ca*, a = 14.267(3), b = 22.494(4), c = 22.116(3) Å, U = 7 079.3(2) $Å^3$, M = 1 071.3, D_m = 2.02 g cm^{-3}, Z = 8, D_c = 2.01 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 38.9 cm^{-1}, $F(000)$ = 4 064.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50° with scan range −0.9 to +1.1° (2θ) around the $K_{\alpha1} - K_{\alpha2}$ angles, scan speed 2—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for 0.25 scan time. Measurements were carried out at ambient temperature. Three standard reflections were monitored every 200 reflections and showed slight changes during data collection; the data were corrected for this. The density was measured by flotation.

Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 2 173 Observed reflections (3 461 total) [$I/\sigma(I) > 3.0$] were used in the refinement, and corrected for Lorentz, polarisation and absorption effects, the last with ABSCOR;[3] maximum and minimum transmission factors were 0.66 and 0.49. The crystal dimensions were 0.35 × 0.87 × 0.12 mm.

Systematic absences *hkl*, $h + k \neq 2n$; *h0l*, $l \neq 2n$; *hk0*, $h \neq 2n$ are consistent with either space group *C2ca* (non-standard setting of *Aba*2) or *Cmca*. The latter was initially selected.

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† Triethylammonium 3,4-μ-chloro-1,1,3,5-tetrachloro-1,1,2,2,3,3,4,4,5,-5-decamethyl-1,2,5;2,3,4;2,4,5-tri-μ_3-oxo-pentastannate.

Supplementary data available (No. SUP 56359, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc. Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

From the density there appeared to be three molecules of the expected toluene-3,4-dithiol adduct in the asymmetric unit. However, the Patterson solution routine of the SHELXTL program indicated at least four heavy atoms. Using four Sn atoms gave $R = 0.40$, and from successive Fourier syntheses one more Sn atom and the remaining atoms of the anion were located. Further refinement led to the chemical identification of the compound.

Refinement converged at $R = 0.059$, but the stoicheiometry required that the main cell content was a monoanion, and a series of residual peaks in the Fourier synthesis could not be interpreted as a cation. Relaxation of the symmetry to *C2ca* removed the mirror plane in the $[(SnMe_2Cl)_5O_3]^-$ anion and revealed an $[NHEt_3]^+$ cation, disordered over two sites. Final refinement was somewhat difficult, no doubt because of the pseudo-symmetry, and it was necessary to include a damping factor. Not unnaturally, the apparent bond lengths and angles in the cation depart somewhat from standard values. Anisotropic thermal parameters were used for atoms of the anion only, and hydrogen atoms were not included. Final refinement was by cascaded least-squares methods to $R = 0.038$. The largest peak on a final difference-Fourier synthesis was of height 1.2 e Å^{-3}, with the highest 10 peaks close to Sn atoms. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0008$ was used. This was shown to be satisfactory by a weight analysis. Computing was with the SHELXTL[4] system on a Data General NOVA 3 computer, following initial processing on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 5.

Table 1. Atomic co-ordinates (× 10^4)

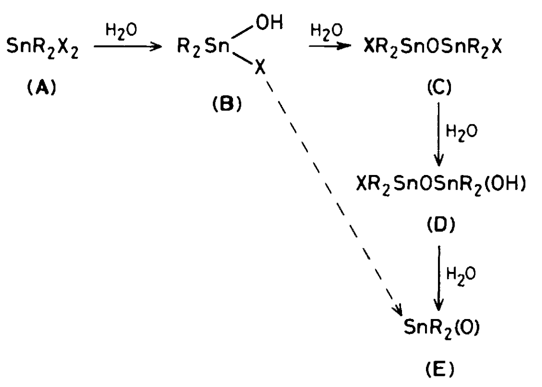
Atom	*x*	*y*	*z*
Sn(1)	5 000	7 696(1)	5 304(1)
Sn(2)	4 976(3)	9 072(1)	4 348(1)
Sn(3)	4 983(3)	6 246(1)	4 996(1)
Sn(4)	4 999(3)	7 518(1)	3 816(1)
Sn(5)	4 986(3)	6 548(1)	6 587(1)
Cl(1)	5 023(15)	5 469(2)	5 996(2)
Cl(2)	5 109(12)	8 796(2)	3 199(2)
Cl(3)	5 068(12)	9 186(2)	5 487(2)
Cl(4)	5 042(10)	6 335(2)	3 481(2)
Cl(5)	5 038(11)	7 591(2)	6 917(2)
O(1)	4 875(23)	6 806(4)	5 720(4)
O(2)	4 878(17)	7 076(4)	4 620(4)
O(3)	5 059(24)	8 200(3)	4 470(3)
C(11)	6 340(12)	7 913(8)	5 614(7)
C(12)	3 558(13)	7 872(9)	5 492(8)
C(21)	3 641(27)	9 383(11)	4 287(14)
C(22)	6 388(23)	9 495(14)	4 209(20)
C(31)	3 598(16)	5 920(10)	4 765(11)
C(32)	6 287(17)	5 942(8)	4 840(9)
C(41)	3 537(12)	7 494(7)	3 421(8)
C(42)	6 344(11)	7 638(6)	3 541(6)
C(51)	6 343(18)	6 274(9)	6 809(9)
C(52)	3 571(12)	6 435(8)	6 916(8)
N(1)*	8 605(18)	762(9)	2 599(11)
N(2)*	6 587(28)	695(15)	2 245(16)
C(01)*	9 523(31)	196(21)	2 307(22)
C(02)*	7 808(26)	515(15)	3 110(16)
C(03)*	8 285(25)	1 119(14)	2 152(14)
C(04)*	7 091(49)	314(30)	2 022(32)
C(05)*	7 130(39)	1 298(25)	2 742(26)
C(06)*	5 912(22)	166(12)	2 515(14)
C(101)	9 974(55)	410(8)	2 107(8)
C(102)	7 853(27)	1 044(16)	1 760(18)
C(103)	7 446(26)	815(17)	3 342(17)

* 0.5 Occupancy.

As well as revealing the cation, use of the lower symmetry space group has produced shifts out of the mirror plane of three of the tin atoms by 5 to 10σ, of one chlorine by 10σ, and of two of the oxygen atoms by 5 to 8σ. These effects support the *C2ca* space group assignment. Final atomic co-ordinates are given in Table 1 and bond lengths and angles in Table 2.

Results and Discussion

The hydrolysis of SnR_2X_2 species can be viewed as a stepwise process giving rise to a variety of intermediates,[2] see Scheme. Species (**E**) is obtained directly when R is bulky (*e.g.* t-butyl) in which case the formation of (**C**) is prevented. Our product (**1**) fits logically into such a sequence, though pentamers have not



Scheme.

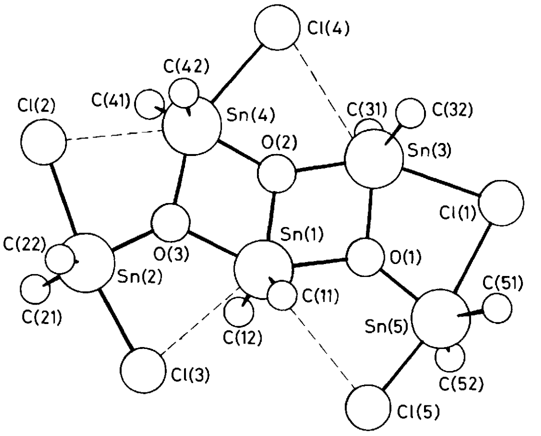


Figure 1. View of the $[(SnMe_2Cl)_5O_3]^-$ ion, showing the atomic numbering scheme

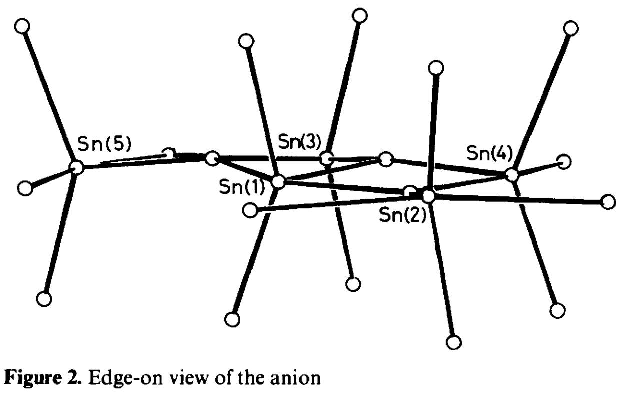


Figure 2. Edge-on view of the anion

Table 2. Bond lengths (Å) and selected bond angles (°)*

Sn(1)–O(1)	2.212(9)	Sn(3)–Cl(1)	2.820(4)	Sn(5)–Cl(1)	2.756(4)	N(1)–C(01)	1.937(52)
Sn(1)–O(2)	2.064(8)	Sn(3)–O(1)	2.044(9)	Sn(5)–Cl(5)	2.459(4)	N(1)–C(02)	1.696(43)
Sn(1)–O(3)	2.165(7)	Sn(3)–O(2)	2.049(8)	Sn(5)–O(1)	2.009(9)	N(1)–C(03)	1.353(40)
Sn(1)–C(11)	2.088(17)	Sn(3)–C(31)	2.169(24)	Sn(5)–C(51)	2.090(25)	C(01)–C(101)	0.918(72)
Sn(1)–C(12)	2.137(19)	Sn(3)–C(32)	2.012(24)	Sn(5)–C(52)	2.160(18)	C(02)–C(103)	0.992(51)
Sn(2)–Cl(2)	2.622(4)	Sn(4)–Cl(4)	2.763(4)	Cl(2) • • • Sn(4)	3.186(4)	C(03)–C(102)	1.077(52)
Sn(2)–Cl(3)	2.537(4)	Sn(4)–O(2)	2.044(8)	Cl(3) • • • Sn(1)	3.378(4)	N(2)–C(04)	1.223(78)
Sn(2)–O(3)	1.983(8)	Sn(4)–O(3)	2.111(7)	Cl(4) • • • Sn(3)	3.357(4)	N(2)–C(05)	1.912(51)
Sn(2)–C(21)	2.034(37)	Sn(4)–C(41)	2.263(18)	Cl(5) • • • Sn(1)	3.575(4)	N(2)–C(06)	1.642(46)
Sn(2)–C(22)	2.249(33)	Sn(4)–C(42)	2.030(16)			C(04)–C(102)	2.053(77)
						C(05)–C(103)	1.774(68)
						C(06)–C(101′)	1.671(71)

O(1)–Sn(1)–O(2)	71.7(3)	Cl(1)–Sn(3)–O(1)	76.7(3)	Cl(1)–Sn(5)–Cl(5)	168.6(2)
O(1)–Sn(1)–O(3)	146.3(3)	Cl(1)–Sn(3)–O(2)	152.2(3)	Cl(1)–Sn(5)–O(1)	78.7(3)
O(1)–Sn(1)–C(11)	98.5(9)	Cl(1)–Sn(3)–C(31)	89.6(8)	Cl(1)–Sn(5)–C(51)	80.5(7)
O(1)–Sn(1)–C(12)	90.5(10)	Cl(1)–Sn(3)–C(32)	84.6(7)	Cl(1)–Sn(5)–C(52)	94.3(6)
O(2)–Sn(1)–O(3)	74.6(3)	O(1)–Sn(3)–O(2)	75.6(3)	Cl(5)–Sn(5)–O(1)	90.5(3)
O(2)–Sn(1)–C(11)	118.4(8)	O(1)–Sn(3)–C(31)	108.9(11)	Cl(5)–Sn(5)–C(51)	100.6(7)
O(2)–Sn(1)–C(12)	100.8(8)	O(1)–Sn(3)–C(32)	114.4(11)	Cl(5)–Sn(5)–C(52)	92.3(6)
O(3)–Sn(1)–C(11)	97.0(10)	O(2)–Sn(3)–C(31)	98.4(9)	O(1)–Sn(5)–C(51)	112.5(11)
O(3)–Sn(1)–C(12)	96.1(10)	O(2)–Sn(3)–C(32)	107.9(8)	O(1)–Sn(5)–C(52)	106.3(11)
C(11)–Sn(1)–C(12)	140.7(7)	C(31)–Sn(3)–C(32)	133.4(8)	C(51)–Sn(5)–C(52)	138.7(8)
O(3)–Sn(2)–C(21)	113.8(13)	Cl(4)–Sn(4)–O(2)	76.5(2)	Sn(1)–O(3)–Sn(2)	129.2(4)
O(3)–Sn(2)–C(22)	112.6(13)	Cl(4)–Sn(4)–O(3)	152.1(2)	Sn(1)–O(3)–Sn(4)	101.6(3)
Cl(2)–Sn(2)–Cl(3)	169.4(4)	Cl(4)–Sn(4)–C(41)	83.9(5)	Sn(2)–O(3)–Sn(4)	128.5(4)
Cl(2)–Sn(2)–O(3)	83.9(2)	Cl(4)–Sn(4)–C(42)	91.6(5)	C(01)–N(1)–C(02)	117.4(21)
Cl(2)–Sn(2)–C(21)	94.9(9)	O(2)–Sn(4)–O(3)	76.2(3)	C(01)–N(1)–C(03)	112.0(25)
Cl(2)–Sn(2)–C(22)	84.5(12)	O(2)–Sn(4)–C(41)	104.3(8)	C(02)–N(1)–C(03)	117.0(25)
Cl(3)–Sn(2)–O(3)	87.8(2)	O(2)–Sn(4)–C(42)	114.0(8)	C(04)–N(2)–C(05)	119.4(45)
Cl(3)–Sn(2)–C(21)	94.6(9)	O(3)–Sn(4)–C(41)	108.6(10)	C(04)–N(2)–C(06)	89.1(39)
Cl(3)–Sn(2)–C(22)	92.6(12)	O(3)–Sn(4)–C(42)	94.0(10)	C(05)–N(2)–C(06)	122.9(29)
C(21)–Sn(2)–C(22)	133.2(11)	C(41)–Sn(4)–C(42)	139.3(6)	N(1)–C(02)–C(103)	118.1(35)
Sn(1)–O(1)–Sn(3)	103.0(4)	Sn(1)–O(2)–Sn(3)	108.2(4)	N(1)–C(03)–C(102)	133.4(36)
Sn(1)–O(1)–Sn(5)	130.8(5)	Sn(1)–O(2)–Sn(4)	107.5(4)	N(2)–C(05)–C(103)	95.6(30)
Sn(3)–O(1)–Sn(5)	124.3(5)	Sn(3)–O(2)–Sn(4)	142.1(5)	N(2)–C(06)–C(101′)	114.4(22)
				C(02)–C(103)–C(05)	99.3(38)

* Primed atoms are related to unprimed ones by $x - 0.5, y, 0.5 - z$.

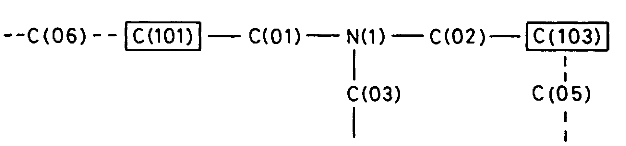
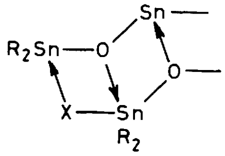


Figure 3. Schematic illustration of the disordered cation. Boxed atoms have 1.0 and other atoms 0.5 occupancy. Full bond lines connect the atoms of one alternative cation position and dashed bond lines connect those of the other position

previously been characterised. It is also novel in being an anion, and its existence suggests that the range of possible hydrolysis products may include many more charged compounds.

Similar compounds that have been examined by *X*-ray methods show the so called 'ladder' structure[6–8] shown below.



As can be seen from Figure 1, the anion of (**1**) shows this ladder structure for its central three tin atoms. Each tin atom is bound to five neighbouring atoms in distorted trigonal-bipyramidal arrangements. The oxygen atoms are trigonally co-ordinated to tin atoms with bond distances in the range 1.98—2.20 Å. These reflect fairly strong co-ordination within the unit, and correspond to Sn–O bonds in other dioxostannanes. Interestingly only one chlorine atom appears to be involved in a halogen bridge: Cl(1) bridges between Sn(5) and Sn(3) (Sn–Cl 2.756 and 2.820 Å respectively). The other chlorine atoms are primarily attached to one tin atom each, though they also form secondary bonds to neighbouring tin atoms (Sn–Cl 3.19—3.58 Å), increasing the co-ordination of these atoms to six or seven.

The anion has near but not exact mirror symmetry (Figure 2), with the principal distortion being a slight bowing from one end to the other. The projection of the methyl groups on each side of the anion gives it a strongly hydrophobic envelope, and

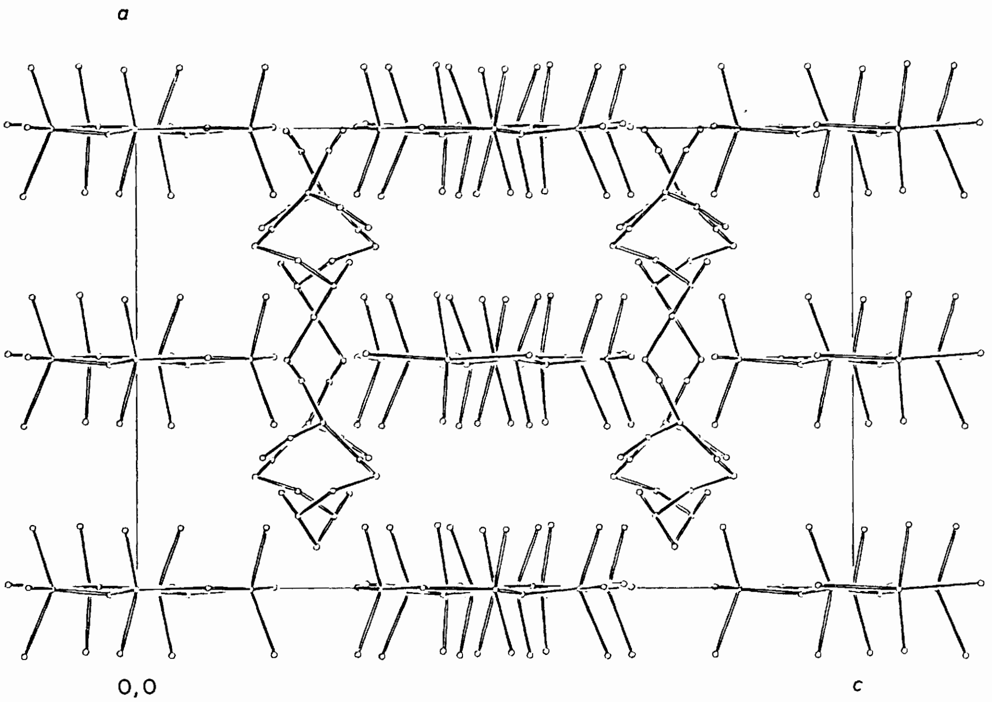


Figure 4. Packing diagram, viewed down *b*

prevents any hydrogen bonding which might be expected between the $[NHEt_3]^+$ ions and the oxygen or chlorine atoms of the anion. As a consequence, the anions occupy two alternative positions (Figure 3), effectively producing infinite chains through the structure. In the crystal (Figure 4) these run in the *a* direction perpendicular to the *b*–*c* planes containing the anions, whose intermolecular contacts are essentially between their methyl groups.

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