Crown Thioether Chemistry of Tin(IV): Formation and Crystal and Molecular Structures of $3SnCl_4{\cdot}2[9]aneS_3$ and $2SnCl_4{\cdot}[18]aneS_6{\cdot}MeCN$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane; $[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane)†

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Reactions of tin(IV) chloride with selected thiacrown ligands in acetonitrile have been studied. With $[9]aneS_3$ (1,4,7-trithiacyclononane) the yellow compound $3SnCl_4{\cdot}2[9]aneS_3$ has been isolated and structurally characterised by X-ray diffraction: orthorhombic, space group *Pbca*, a = 11.245(5) Å, b = 12.927(6) Å, c = 23.779(10) Å, Z = 4, at 230(2) K. The structure consists of six-co-ordinate $[SnCl_3([9]aneS_3)]^+$ cations and $[SnCl_6]^{2-}$ anions in the ratio 2:1. In the cation the thiacrown is chelated facially to a $SnCl_3$ unit with Sn–Cl 2.369(4) (mean), Sn–S 2.637(4) Å (mean). The $[SnCl_6]^{2-}$ counter anions exhibit a regular octahedral geometry with Sn–Cl 2.448(4) (mean) Å. The reaction with $[18]aneS_6$ (1,4,7,10,13,16-hexathiacyclooctadecane) provides yellow crystals of the adduct $2SnCl_4{\cdot}[18]aneS_6{\cdot}$MeCN the structure of which has also been determined by X-ray diffraction; monoclinic, space group *C*2, a = 16.901(5), b = 12.968(5), c = 7.284(3) Å, β = 100.50(3)°, Z = 2, at 240(2) K. The structure consists of two $SnCl_4$ units located at opposite ends of the ring cavity with one above and the other below the ring plane. Each tin atom is six-co-ordinate and is attached to the ring *via cis* chelation of two sulfur atoms.

Crown ether complexes of inorganic tin(IV) and organotin(IV) halides are now well established in the literature. Examples include $SnCl_4(H_2O)_2{\cdot}18$-crown-$6{\cdot}2H_2O{\cdot}CHCl_3$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane),[1] $SnCl_4(H_2O)_2{\cdot}18$-crown-$6{\cdot}2H_2O$,[2] $SnMe_2Cl_2(H_2O){\cdot}18$-crown-6,[3] $SnMe_2(NCS)_2(H_2O)_2{\cdot}18$-crown-6,[4] $SnCl_4(H_2O)_2{\cdot}15$-crown-5 (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane)[5] and $[SnMe_2Cl_2(H_2O)]_2{\cdot}1,3$-xylyl-18-crown-5 (1,3-xylyl-18-crown-5 = 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclooctadecane).[6] Perhaps the most distinguishing structural feature of these hydrated complexes is that there is no direct crown ligand attachment to the metal. Instead the tin atom is held in a peripheral location by hydrogen bonding of the type $O_{crown}\cdots H_2O{-}M$ involving co-ordinated water molecule(s), *i.e.* second-sphere ligation. Treatment of $SnCl_4$ and 18-crown-6 under strictly anhydrous conditions yields the six-co-ordinate 1:1 adduct incorporating direct ligand binding but with only two of the available ring oxygen atoms co-ordinated to the metal.[7] In the reaction of $SnCl_4$ with 15-crown-5 in acetonitrile degradation of the ring takes place with elimination of dichloromethane and formation of the molecular compound of composition $SnCl_2(C_8H_{16}O_5){\cdot}SnCl_4$.[8]

Surprisingly there are no reports of tin(IV) complexation with the analogous crown thioether ligands despite the extensive recognition and coverage of Sn–S bonds in tin chemistry.[9] Encouraged by the fact that S-donor macrocyclic ligands show little or no affinity for hydrogen-bond interactions, *e.g.* the crown ether–oxonium ion complex $[H_3O(18\text{-crown-}6)]^+$ [10] has no sulfur counterpart and second-sphere ligation ($S_{crown}\cdots H_2O{-}M$) to a metal ion would seem highly improbable, we are now examining the host–guest structural chemistry of thiamacrocycles with halides and organohalides of Sn^{IV}. In this first report we describe the formation and structural details of the two new tin(IV) compounds $3SnCl_4{\cdot}2[9]aneS_3$ **1** ($[9]aneS_3$ = 1,4,7-trithiacyclononane) and $2SnCl_4{\cdot}[18]aneS_6$ **2** ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane.

Experimental

Manipulations of materials were carried out using a standard Schlenk system and/or a dinitrogen glove-box. All solvents were stored over CaH_2 and distilled under a dinitrogen atmosphere prior to use. The compounds $SnCl_4$ and $[18]aneS_6$ were used as obtained commercially (Aldrich); $[9]aneS_3$ was prepared as reported previously.[11] The IR spectra were recorded on a Perkin Elmer 580B instrument with samples as Nujol mulls placed between CsI discs. Microanalyses were performed by Medac Ltd., Uxbridge, Middlesex.

Preparation of the Complexes.—(*a*) $3SnCl_4{\cdot}2[9]aneS_3$ **1**. Acetonitrile (30 cm³) was placed in an adapted U-tube vessel under a dinitrogen atmosphere. Tin(IV) chloride (0.155 g, 0.595 mmol) in MeCN (10 cm³) was added dropwise to one side-arm and $[9]aneS_3$ (0.107 g, 0.594 mmol) in MeCN (10 cm³) was similarly added to the other. On leaving the system undisturbed for several days colourless, rectangular crystals deposited on the walls of the vessel. After removal of the mother-liquors the product was collected carefully, washed with hexane (2 × 10 cm³) and dried *in vacuo*. Yield 0.097 g, 43% (Found: C, 12.45; H, 2.10; Cl, 37.05. Calc. for $C_{12}H_{24}Cl_{12}S_6Sn_3$: C, 12.60; H, 2.10; Cl, 37.25%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1304w, 1289w, 1143s, 1081w, 971w, 929m, 891s, 821s, 661w, 436m, 345vs (br) and 295vs (br).

(*b*) $2SnCl_4{\cdot}[18]aneS_6{\cdot}MeCN$ **2**. The reaction of $SnCl_4$ (0.140 g, 0.538 mmol) and $[18]aneS_6$ (0.192 g, 0.534 mmol) was carried out following the procedures described in (*a*). The product was obtained as small colourless cubic crystals which were washed with hexane (2 × 10 cm³) and dried *in vacuo*. Yield 0.092 g, 39% (Found: C, 18.10; H, 2.90; Cl, 30.30; N, 1.75. Calc. for $C_{14}H_{27}Cl_8NS_6Sn_2$: C, 18.20; H, 2.95; Cl, 30.75; N, 1.50%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1295w, 1262m, 1225m, 1205s, 1152m, 1130w, 1015w, 915m, 901m, 855s, 739s, 692w, 685s, 644w, 443m, 340 (sh), 330 (sh), 321vs (br), 272s (br) and 251 (sh).

(*c*) The reactions of $SnCl_4$ (0.185 g, 0.710 mmol) with $[12]aneS_4$ (1,4,7,10-tetrathiacyclododecane) (0.171 g, 0.710 mmol) and with $[15]aneS_5$ (1,4,7,10,13-pentathiacyclopentadecane) (0.213 g, 0.710 mmol) were carried out following the procedures described in (*a*) No crystal deposition was observed in either case. Removal of solvent provided residues

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

from which the appropriate starting ligand was recovered unchanged.

X-Ray Crystallography.—Crystal data. $C_{12}H_{24}Cl_{12}S_6Sn_3$, M = 1142.18, orthorhombic, space group *Pbca*, a = 11.245(5), b = 12.927(6), c = 23.779(10) Å, U = 3457(3) Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 0.710 73 Å), Z = 4, D_c = 2.20 g cm^{-3}, F(000) = 2184. Colourless, air-sensitive plate. Crystal dimensions: 0.20 × 0.20 × 0.09 mm, μ(Mo-Kα) = 3.45 mm^{-1}.

$C_{12}H_{24}Cl_8S_6Sn_2{\cdot}CH_3CN$, M = 922.7, monoclinic, space group *C*2, a = 16.901(5), b = 12.968(5), c = 7.284(3) Å, β = 100.50(3)°, U = 1569.7(10) Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflections, λ = 0.710 73 Å), Z = 2, D_c = 1.95 g cm^{-3}, F(000) = 894. Colourless, air-sensitive block. Crystal dimensions: 0.14 × 0.13 × 0.07 mm, μ(Mo-Kα) = 2.68 mm^{-1}.

Data collection and processing. Siemens R3m four-circle diffractometer in the ω–2θ mode to maximum 2θ of 50°, graphite-monochromated Mo-Kα radiation. Gaussian absorption (maximum, minimum transmission factors = 0.70, 0.64) correction applied for compound **1**. Three standard reflections were monitored every 200: the data were rescaled to correct for the slight changes which occurred during data collection. For compound **1**, T = 230 K, 3043 unique reflections (h 0–13, k 0–15, l 0–28); for **2**, T = 240 K, 2267 unique reflections (h −12 to 20, k −12 to 15, l −8 to 8).

Structure analysis and refinement. Direct methods followed by a full-matrix least-squares refinement on F^2 for all data (using SHELXL 93).[12] Hydrogen atoms were added at calculated positions and refined using a riding model. The weighting scheme used is defined as $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$ where $P = [\max(F_o^2, O) + 2F_c^2]/3$. For compound **1**, goodness of fit on F^2 = 0.937, $R1$ [for $I > 2\sigma(I)$] = 0.0645 and $wR2$ (for all data) = 0.1548, weighting coefficients are a = 0.0662 and b = 0.00; for **2**, goodness of fit on F^2 = 1.070, $R1$ [for $I > 2\sigma(I)$] = 0.0455 and $wR2$ (for all data) = 0.1102, weighting coefficients are a = 0.0444 and b = 10.03.

Programs and computers used and sources of scattering factor data are given in ref. 13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The structure of $3SnCl_4{\cdot}2[9]aneS_3$ **1** consists of discrete $[SnCl_3([9]aneS_3)]^+$ cations and $[SnCl_6]^{2-}$ anions in the ratio 2:1. The fractional atomic coordinates are given in Table 1, selected bond lengths and angles in Table 2 and torsion angles around the thiacrown ring in Table 3. The cation, which is illustrated in Fig. 1 with the atom numbering used, incorporates terdentate co-ordination of $[9]aneS_3$ to a $SnCl_3{}^+$ unit with a resulting *fac*-octahedral metal geometry. It also provides a rare example of thioether-induced anion expulsion. As a general rule crown thioethers, owing to their low σ-donor ability, seldom displace counter ions such as halides from the co-ordination sphere of a metal ion.[14] In the present instance however the six-co-ordinate preference of Sn^{IV} and the conformational (endodentate) preference of the ligand act in concert to provide a six-co-ordinate cationic $SnCl_3{}^+$ species rather than a seven-co-ordinate neutral adduct (1 : 1) of $SnCl_4$. The released chloride ions co-ordinate to a further molecule of tin(IV) chloride to provide the $[SnCl_6]^{2-}$ counter anions. The Sn–Cl bond distances of the $SnCl_3{}^+$ unit are equivalent [2.366(4)–2.371(4), mean 2.369(4) Å] and are perceptibly shorter than those in the neutral six-co-ordinate S-donor adducts $SnCl_4{\cdot}2L$ [L = 1,5-dithiacyclooctane) (mean Sn–Cl 2.421 Å)[15] or 1,3-diethylthiourea (mean Sn–Cl 2.43 Å)[16]]. The Sn–S bond distances are also equivalent [2.618(3)–2.657(4), mean 2.637(4) Å] reflecting the symmetrical disposition of the trio of sulfur and halogen atoms around the central metal. The angular constriction imposed by $[9]aneS_3$(S–Sn–S mean 83.3°) is counterbalanced by a corresponding angular dilation between the chlorine atoms (Cl–Sn–Cl mean 98.6°). A similar macrocyclic constriction/dilation effect has been noted in $VOCl_2{\cdot}[9]aneS_3$[17] (S–V–S mean 81.0, Cl–V–Cl 95.0, Cl–V–O mean 104.8°) and $ReO_3{\cdot}[9]aneS_3$[18] (S–Re–S mean 79.5, O–Re–O mean 107.4°). Within

Table 1 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Sn(1)	144(1)	4644(1)	1882(1)
Sn(2)	0	5000	5000
Cl(1)	−1083(3)	6113(3)	1742(2)
Cl(2)	−192(3)	4289(3)	2844(2)
Cl(3)	1939(3)	5590(3)	1968(2)
Cl(4)	−1744(3)	5604(3)	4476(2)
Cl(5)	319(3)	6777(3)	5326(2)
Cl(6)	1248(3)	5334(3)	4180(2)
S(1)	451(3)	4543(3)	775(2)
S(4)	1458(3)	2972(3)	1863(2)
S(7)	−1625(3)	3365(3)	1669(2)
C(2)	1415(10)	3403(10)	688(5)
C(3)	2203(10)	3151(11)	1180(6)
C(5)	352(10)	1952(9)	1711(6)
C(6)	−891(11)	2198(10)	1937(6)
C(8)	−1590(11)	3179(10)	902(6)
C(9)	−1039(10)	4109(10)	562(6)

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Sn(1)–Cl(2)	2.366(4)	Sn(1)–S(4)	2.618(3)
Sn(1)–Cl(3)	2.369(3)	Sn(1)–S(7)	2.636(3)
Sn(1)–Cl(1)	2.371(4)	Sn(1)–S(1)	2.657(4)
Cl(2)–Sn(1)–Cl(3)	98.79(13)	Cl(1)–Sn(1)–S(7)	92.10(13)
Cl(2)–Sn(1)–Cl(1)	101.38(13)	S(4)–Sn(1)–S(7)	84.54(11)
Cl(3)–Sn(1)–Cl(1)	95.40(13)	Cl(2)–Sn(1)–S(1)	165.88(12)
Cl(2)–Sn(1)–S(4)	86.93(12)	Cl(3)–Sn(1)–S(1)	90.01(12)
Cl(3)–Sn(1)–S(4)	86.97(12)	Cl(1)–Sn(1)–S(1)	88.67(13)
Cl(1)–Sn(1)–S(4)	170.87(14)	S(4)–Sn(1)–S(1)	82.51(11)
Cl(2)–Sn(1)–S(7)	86.76(12)	S(7)–Sn(1)–S(1)	82.94(11)
Cl(3)–Sn(1)–S(7)	169.60(12)		

Table 3 Torsion angles (°) around the thia crown ring

C(2)–C(3)–S(4)–C(5)	55.52(1.13)
C(3)–S(4)–C(5)–C(6)	−132.99(1.00)
S(4)–C(5)–C(6)–S(7)	60.69(1.24)
C(5)–C(6)–S(7)–C(8)	54.77(1.10)
C(6)–S(7)–C(8)–C(9)	−127.12(0.88)
S(7)–C(8)–C(9)–S(1)	53.59(1.22)
C(8)–C(9)–S(1)–C(2)	59.46(1.11)
C(9)–S(1)–C(2)–C(3)	−131.22(0.95)
S(1)–C(2)–C(3)–S(4)	55.38(1.24)

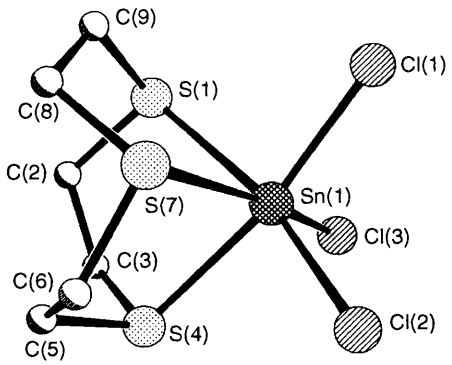

Fig. 1 View of the $[SnCl_3([9]aneS_3)]^+$ cation with atom labelling

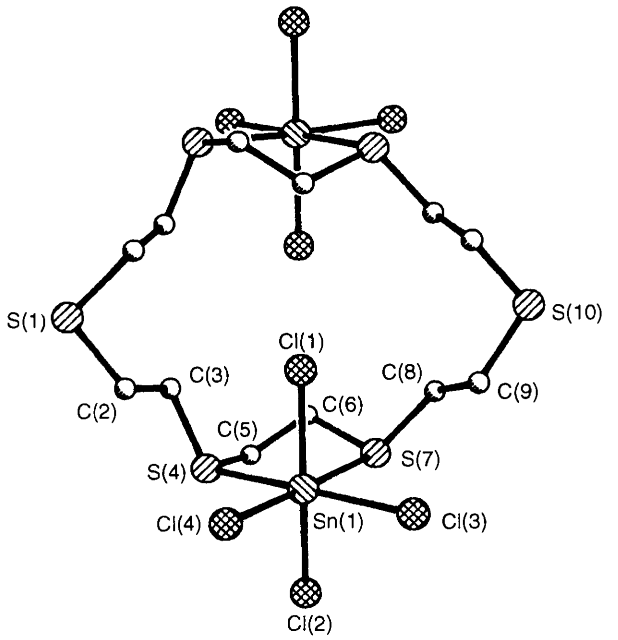

Fig. 2 Molecular structure of $2SnCl_4$·[18]aneS_6 with atom labelling

Table 4 Atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Sn(1)	2 292(1)	6 983(5)	1 883(1)
Cl(1)	922(1)	6 981(12)	2 430(3)
Cl(2)	3 513(1)	7 001(13)	662(3)
Cl(3)	2 636(11)	8 564(16)	3 494(21)
Cl(4)	2 737(11)	5 890(14)	4 363(31)
Cl(3′)	2 707(11)	8 051(14)	4 398(25)
Cl(4′)	2 613(10)	5 352(12)	3 470(28)
S(1)	218(9)	3 533(13)	1 781(21)
C(2)	1 061(24)	4 355(44)	1 551(66)
C(2′)	494(18)	4 570(28)	−2 465(39)
C(3)	965(13)	4 948(20)	−460(40)
S(4)	1 963(8)	5 485(9)	−362(21)
C(5)	1 725(8)	6 139(12)	−2 577(21)
C(6)	1 227(6)	7 070(22)	−2 535(13)
S(7)	1 774(10)	8 133(12)	−1 168(23)
S(4′)	1 792(10)	5 859(12)	−1 213(24)
S(7′)	1 970(12)	8 529(14)	−311(32)
C(8)	1 055(15)	9 048(23)	−361(36)
C(9)	1 060(21)	9 619(35)	1 711(50)
S(10)	163(9)	10 375(11)	1 812(29)
C(9′)	564(25)	9 526(37)	−2 258(51)
N(21)	0	4 698(38)	−5 000
C(21)	0	3 843(42)	−5 000
C(22)	0	2 603(40)	−5 000
N(31)	0	9 081(39)	−5 000
C(31)	0	9 952(40)	−5 000
C(32)	0	11 157(40)	−5 000

Pairs of disordered atom sites are labelled with primed and non-primed numbers.

the ligand there is no evidence of distortion. The regularity of the C–C (mean 1.54 Å) and S–C (mean 1.84 Å) bond distances is matched by the regular $a^{-}gga^{-}gga^{-}gg$ pattern of torsion angles around the ring. The central metal atom is displaced by 1.689(2) Å from the plane defined by the three sulfur atoms and by 1.146(2) Å from that of the three chlorine atoms. The two planes cross at 3.9(0.2)°. The $[SnCl_6]^{2-}$ anions exhibit regular octahedral geometry with Sn–Cl [mean 2.448(4) Å] *cf.* $[SMe_3]_2[SnCl_6]$[19] (Sn–Cl mean 2.420 Å).

Table 5 Selected bond lengths (Å) and angles (°) for compound **2**

Sn(1)–Cl(3′)	2.30(2)	C(2)–C(3)	1.64(3)
Sn(1)–Cl(4)	2.31(2)	C(3)–S(4)	1.81(2)
Sn(1)–Cl(3)	2.38(2)	S(4)–C(5)	1.80(2)
Sn(1)–Cl(2)	2.391(2)	C(5)–C(6)	1.48(2)
Sn(1)–Cl(1)	2.421(2)	C(6)–S(7)	1.85(3)
Sn(1)–Cl(4′)	2.42(2)	S(7)–C(8)	1.87(2)
Sn(1)–S(4)	2.535(10)	C(8)–C(9)	1.68(2)
Sn(1)–S(7′)	2.56(2)	C(9)–S(10)	1.82(2)
Sn(1)–S(7)	2.687(13)	N(31)–C(31)	1.13(2)
Sn(1)–S(4′)	2.689(13)	C(31)–C(32)	1.56(2)
S(1)–C(2)	1.81(2)		
Cl(4)–Sn(1)–Cl(3)	97.3(7)	Cl(2)–Sn(1)–Cl(1)	167.85(8)
Cl(4)–Sn(1)–Cl(2)	96.7(5)	Cl(4)–Sn(1)–S(4)	92.1(7)
Cl(3)–Sn(1)–Cl(2)	91.5(5)	Cl(3)–Sn(1)–S(4)	169.4(6)
Cl(4)–Sn(1)–Cl(1)	93.2(5)	Cl(1)–Sn(1)–S(4)	90.0(4)
Cl(3)–Sn(1)–Cl(1)	94.3(5)	S(4)–Sn(1)–S(7)	83.8(5)

Pairs of disordered atom sites are labelled with primed and non-primed numbers.

The structure of $2SnCl_4$·[18]aneS_6·MeCN **2** is shown in Fig. 2 together with the atom labelling scheme. The fractional atomic coordinates are given in Table 4, selected bond distances and angles in Table 5. In this neutral molecule the hexathia crown acts as a bidentate (S,S′) chelating ligand to each of two separate $SnCl_4$ units located at opposite ends of the cavity and on opposite sides of the ring plane. Again the six-co-ordinate geometry favoured by Sn^{IV} is preserved at the expense of limited ring attachment as witnessed in the corresponding crown ether compound $SnCl_4$·18-crown-6.[7] The Sn–S bond distances lie in the range 2.535(10)–2.689(13), mean 2.618(12) Å, and are similar to those in **1**, mean 2.637(4) Å, and other octahedral $SnCl_4$·2L complexes *viz.*, L = 1,5-dithiacyclooctane, Sn–S 2.602(1).[15] Compound **2** is highly disordered and the hexathia ring shows appreciable distortion in order to accommodate the two $SnCl_4$ units. To a first approximation the asymmetric unit comprises the labelled atoms in Fig. 2, and a two-fold rotation about the axis from S(1) to S(10) generates the rest of the molecule. Each of the atoms Cl(3), Cl(4), S(4), S(7), C(2), C(9), S(1) and S(10) occupies two sites with site occupancy factors of 0.5. This situation may be envisaged by twisting the asymmetric unit about the Cl(1)–Sn(1)–Cl(2) axis whilst keeping atoms C(3) and C(8) fixed; the expected disorder for atoms C(5) and C(6) could not be modelled in a satisfactory manner. An overall effect of this disorder is that the two-fold axis does not actually pass through S(1) and S(10) but lies midway between these atoms and their disordered positions (the two-fold axis is at 0, *y*, 0). Additionally the structure contains poorly defined disordered solvent acetonitrile. The resulting *trans*-obverse arrangement in **2** has been previously observed in $2SbCl_3$·[18]aneS_6[20] which, however, features terdentate attachment to each individual $SbCl_3$ moiety. Attempts to isolate the terdentate structural analogue $2SnCl_4$·[18]aneS_6≡ $[2SnCl_3{}^{+}$·[18]ane$S_6][SnCl_6{}^{2-}]$ *via* chloride expulsion as induced by a large excess of tin(IV) chloride (5 : 1) have proved unsuccessful.

Acknowledgements

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References

1 P. A. Cusack, B. N. Patel, P. J. Smith, D. W. Allen and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1984, 1239.
2 G. Valle, A. Cassol and U. Russo, *Inorg. Chim. Acta*, 1984, **82**, 81.
3 M. M. Amini, A. L. Rheingold, R. W. Taylor and J. J. Zuckermann, *J. Am. Chem. Soc.*, 1984, **106**, 7289.
4 G. Valle, G. Ruisi and U. Russo, *Inorg. Chim. Acta*, 1985, **99**, L21.
5 E. Hough, D. G. Nicholson and A. K. Vasudevan, *J. Chem. Soc., Dalton Trans.*, 1986, 2335.

6 A. Mitra, C. B. Knobler and S. E. Johnson, *Inorg. Chem.*, 1993, **32**, 1076.

7 S. G. Bott, H. Prinz, A. Alvanipour and J. L. Atwood, *J. Coord. Chem.*, 1987, **16**, 303.

8 V. K. Bel'skii, B. M. Bulychev, N. R. Strel'tsova, P. A. Storozhenko and L. V. Ivakina, *Dokl. Acad. Nauk. SSSR*, 1988, **303**, 1137.

9 A. G. Davies and P. J. Smith, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon, Oxford, 1982, vol. 2. ch. 11.

10 See *e.g.* R. Chênevert, D. Chamberland, M. Simard and F. Brisse, *Canad. J. Chem.*, 1990, **68**, 797; J. L. Atwood, S. G. Bott, C. M. Means, A. W. Coleman, H. Zhang and M. T. May, *Inorg. Chem.*, 1990, **29**, 467.

11 P. J. Blower and S. R. Cooper, *Inorg. Chem.*, 1987, **26**, 2009.

12 G. M. Sheldrick, *J. Appl. Crystallogr.*, 1993, in the press.

13 G. R. Willey, A. Asab, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1993, 365.

14 S. R. Cooper and S. C. Rawle, *Struct. Bonding* (*Berlin*), 1990, **72**, 1.

15 M. M. Olmstead, K. A. Williams and W. K. Musker, *J. Am. Chem. Soc.*, 1982, **104**, 5567.

16 D. Tudela, M. A. Khan and J. J. Zuckermann, *J. Chem. Soc., Dalton Trans.*, 1991, 999.

17 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 1414.

18 H.-J. Küppers, B. Nuber, J. Weiss and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1990, 979.

19 O. Knop, A. Linden, B. R. Vincent, S. C. Choi, T. S. Cameron and R. J. Boyd, *Can. J. Chem.*, 1989, **67**, 1984.

20 G. R. Willey, M. T. Lakin, M. Ravindran and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 271.

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