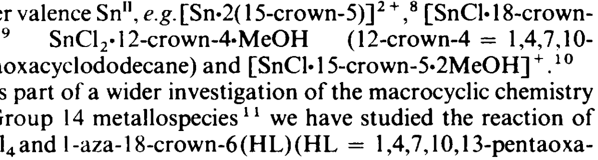
Formation of Azacrown Complexes of Tin(IV): Crystal and Molecular Structure of $[H_2L]_2[SnCl_5(H_2O)]_2{\cdot}H_2O{\cdot}MeCN$ (HL = 1,4,7,10,13-pentaoxa-16-azacyclooctadecane)†

Gerald R. Willey,* Martin D. Rudd and Nathaniel W. Alcock
Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

Reaction of $SnCl_4$ and aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane, HL) provides the white solid $SnCl_3L$ **1** with elimination of HCl. Analytical and spectroscopic characterisation of **1** points to a structure in which a $SnCl_3$ unit is bonded to the deprotonated nitrogen atom and the two adjacent oxygen atoms of the azacrown. Partial hydrolysis of **1** during an attempted recrystallisation in acetonitrile, gave colourless crystals of the ionic compound $[H_2L]_2[SnCl_5(H_2O)]_2{\cdot}H_2O{\cdot}MeCN$ **2** the structure of which was determined by X-ray diffraction: monoclinic, space group $C2/m$, $a = 40.15(2)$, $b = 12.231(6)$, $c = 10.019(7)$ Å, $\beta = 104.05(5)°$, $Z = 4$. Two independent azacrown molecules are both protonated. Molecule 1 has the solvate water molecule located centrally over the ring cavity, held by three strong $O{-}H_{water}\cdots O_{ring}$ 2.793 and $O_{water}\cdots H{-}N_{ring}$ 2.690 Å hydrogen bonds; molecule 2 behaves as a second-sphere ligand to two separate six-co-ordinate $[SnCl_5(H_2O)]^-$ anions positioned on opposite sides of the ring. The co-ordinated H_2O molecules are located over the centre of the azacrown ligand and are involved in hydrogen bonding to the nitrogen and oxygen atoms of the ring.

Within the p-block elements interest in tin-(II) and -(IV) oxa, thia- and aza-macrocyclic derivatives has been spasmodic. Although several crown ether complexes of tin halides and pseudohalides had been isolated and spectroscopically evaluated earlier,[1] the first real focus on the structural chemistry of such compounds dates from 1984 with the crystal structure determinations of $SnCl_4(H_2O)_2{\cdot}18\text{-crown-6}{\cdot}2H_2O{\cdot}CHCl_3$,[2] $SnCl_4(H_2O)_2{\cdot}18\text{-crown-6}{\cdot}2H_2O$[3] and $[SnMe_2Cl_2(H_2O)]_2{\cdot}18\text{-crown-6}$.[4] In all three examples 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) acts as a second-sphere ligand and is bound indirectly to the metal *via* extensive hydrogen bonding of the type $O_{crown}\cdots H_2O{-}Sn$. A similar pattern was subsequently identified in other octahedral tin(IV) complexes, *e.g.* $SnMe_2(NCS)_2(H_2O)_2{\cdot}18\text{-crown-6}$[5] and $SnCl_4(H_2O)_2{\cdot}15\text{-crown-5}$ (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane).[6] Interestingly 18-crown-6 and $SnCl_4$ react under strictly anhydrous conditions to provide the 1 : 1 six-co-ordinate adduct involving bidentate ligand binding.[7] Encapsulation, in the sense that all available oxygens of the crown are bonded directly to one metal atom located in an extra-cavity position, is only observed with lower valence Sn^{II}, *e.g.* $[Sn{\cdot}2(15\text{-crown-5})]^{2+}$,[8] $[SnCl{\cdot}18\text{-crown-6}]^+$,[9] $SnCl_2{\cdot}12\text{-crown-4}{\cdot}MeOH$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane) and $[SnCl{\cdot}15\text{-crown-5}{\cdot}2MeOH]^+$.[10]

As part of a wider investigation of the macrocyclic chemistry of Group 14 metallospecies[11] we have studied the reaction of $SnCl_4$ and 1-aza-18-crown-6(HL)(HL = 1,4,7,10,13-pentaoxa-16-azacyclooctadecane) as a possible route to encapsulation of Sn^{IV}. We anticipated that a $SnCl_3$ unit might be attached to the ring *via* Sn–N bond formation following aminolysis with release of HCl. Pajerski *et al.*[12] have effected a similar insertion of an R_2Al unit into the ring cavity of HL using the metallation (1). Here the metal is locked into a trigonal-bipyramidal geometry by auxiliary bonding interactions with two oxygen atoms of the ring.



(1)

Experimental

All manipulations were carried out under a dinitrogen atmosphere using a conventional glove-box and standard Schlenk techniques. All solvents were dried over CaH_2 and, subsequently, sodium–benzophenone and distilled under a dinitrogen atmosphere prior to use. Tin tetrachloride and the aza-crown ligand HL were obtained from Aldrich Chemical Co. and used as supplied. Proton (220 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded on a Perkin Elmer R34 spectrometer, IR spectra on a Perkin Elmer 580B spectrophotometer with samples as Nujol mulls placed between CsI plates. Elemental analyses were carried out by Medac, Brunel University, Uxbridge, Middlesex.

Preparation of the Complexes.—(*a*) *Trichloro*(1,4,7,10,13-*pentaoxa*-16-*azacyclooctadecyl*)*tin* $SnCl_3L$ **1**. 1,4,7,10,13-Pentaoxa-16-azacyclooctadecane (0.15 g, 0.57 mmol) in acetonitrile (50 cm^3) was added dropwise to a solution of tin(IV) chloride (0.149 g, 0.57 mmol) in acetonitrile (25 cm^3) and the resulting solution was stirred at 50 °C for 12 h. Removal of the solvent by slow evaporation yielded a semicrystalline white solid which was washed with hexane and dried *in vacuo*. Yield 0.21 g (72%), m.p.$_{uncorr}$ 144–146 °C (Found: C, 29.3; H, 4.8; Cl, 21.8; N, 2.7. $C_{12}H_{24}Cl_3NO_5Sn$ requires C, 29.6; H, 5.0; Cl, 21.8; N, 2.9%); $\tilde{\nu}_{max}/cm^{-1}$ 1651w, 1567vs, 1355m, 1299s, 1288s, 1245s, 1088vs, 947vs, 849s, 839s, 724s, 532m and 321vs (br) (Nujol); $\delta_H(CD_3CN)$ 3.24 (4 H, m, CH_2NCH_2), 3.63 (16 H, m, OCH_2CH_2O) and 3.68 (4 H, m, OCH_2CH_2N); $\delta_C(CD_3CN)$ 70.54 (8C, m, OCH_2CH_2O), 65.14 (2C, s, OCH_2CH_2N) and 45.81 (2C, s, CH_2NCH_2).

(*b*) $[H_2L]_2[SnCl_5(H_2O)]_2{\cdot}H_2O{\cdot}MeCN$ **2**. As an attempted recrystallisation, compound **1** (0.20 g, 0.41 mmol) was dissolved in boiling acetonitrile and filtered to give a clear solution. On

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

cooling this solution in a refrigerator, colourless block *crystals* of the product formed on the walls of the vessel and a white residue was deposited. The crystals were carefully collected, washed with diethyl ether (10 cm^3) and stored in a desiccator. A suitable crystal was selected for X-ray diffraction studies. Yield 0.07 g, m.p.$_{uncorr}$ 106–108 °C; $\tilde{\nu}_{max}/cm^{-1}$ 3520 (br), 3328m, 3159w, 2263m, 1651m, 1600s, 1356m, 1296m, 1277m, 1250m, 1213m, 1103vs, 965m, 947s, 869w, 830s, 791m, 723m, 539m, 480w, 324vs (br) and 308s (Nujol).

X-Ray Crystallography.—Crystal data. $2[C_{12}H_{26}NO_5]^+$ $2[SnCl_5OH_2]^-\cdot H_2O\cdot CH_3CN$, $M = 1215.7$, monoclinic, space group $C2/m$, $a = 40.15(2)$, $b = 12.231(6)$, $c = 10.019(7)$ Å, $\beta = 104.05(5)°$, $U = 4773$ Å^3, $Z = 4$, $D_c = 1.69$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 1.66 mm^{-1}, $T = 290$ K, $R = 0.038$ for 3755 unique observed $[I/\sigma(I) \geqslant 2.0]$ reflections.

A colourless block was mounted in a Lindemann capillary for protection from hydrolysis. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ± 0.7°(ω) around the Kα1-Kα2 angles, scan speed 1.5–15°(ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0–48, 0–14 and − 11 to 11.

Three standard reflections were monitored every 200, and showed a slight decrease during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections ($25 < 2\theta < 27°$). The 4577 reflections were processed using profile analysis to give 4424 unique reflections ($R_{int} = 0.051$), of which 3809 were considered observed $[I/\sigma(I) \geqslant 2.0]$. These were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.38 and 0.80. Crystal dimensions were 0.12 × 0.54 × 0.65 mm.

Systematic reflection conditions *hkl* where $h + k = 2n$ and $0kl$ where $l = 2n$ indicate one of the space groups $C2$, Cm or $C2/m$; the last was initially selected and shown to be correct by the successful refinement. Two independent Sn atoms lying on mirror planes were located by the Patterson interpretation section of SHELXTL PLUS [13] and the light atoms then found by E-map expansion and successive Fourier syntheses. The asymmetric unit contains two half macrocycles, two half anions and one water molecule, all lying on mirror planes. An acetonitrile is disordered across a mirror plane, with only the methyl group significantly displaced from the plane (modelled as a half atom); the disorder of the other atoms shows only as abnormally high U_{22} anisotropic displacement parameters. Atom O(27) in macrocycle 2 is also disordered between two positions, and the adjacent carbon atoms have high U (approximately normal to the ring plane) indicative of unresolved disorder.

Anisotropic thermal parameters were used for all non-H atoms (apart from the disordered atoms which were held isotropic). Hydrogen atoms were given fixed isotropic thermal parameters $U = 0.08$ Å^2. Those defined by the molecular geometry were inserted at calculated positions and not refined. Both O(1) and N(110) had two well marked difference peaks in appropriate positions for hydrogen atoms, indicating the stoichiometry $[C_{12}H_{24}O_5NH_2\cdot H_2O]^+$ for this unit; these hydrogens were not included in the refinement. No firm evidence was found for the protons attached to N(210) in the other ring or in the (presumed) H_2O groups attached to Sn. The position of the nitrogen *vis-a-vis* the oxygen in this ring was also inferred from the satisfactory values of refined thermal parameters.

Table 1 Atom coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Sn(1)	2 233.0(1)	0	1 187.4(3)
Sn(2)	4 149.8(1)	0	5 695.6(4)
Cl(11)	2 240.7(3)	1 946.1(8)	1 251.5(10)
Cl(12)	2 532.8(4)	0	−581.2(15)
Cl(13)	1 669.9(4)	0	−383.9(14)
Cl(14)	2 005.1(4)	0	3 187.0(15)
O(15)	2 744.4(11)	0	2 587.5(40)
Cl(21)	4 114.8(3)	1 956.4(9)	5 579.6(12)
Cl(22)	4 307.0(6)	0	3 564.7(23)
Cl(23)	4 695.9(5)	0	7 238.7(27)
Cl(24)	3 839.0(5)	0	7 478.9(15)
O(25)	3 611.9(11)	0	4 398.0(40)
O(11)	9 960.6(11)	10 000	3 148.6(45)
C(12)	161.8(14)	9 038.6(41)	3 211.5(54)
C(13)	9 934(2)	8 066(4)	2 963(5)
O(14)	9 739.6(9)	8 100.3(25)	1 587.0(31)
C(15)	9 561(2)	7 110(4)	1 155(6)
C(16)	9 342.6(14)	7 256.6(39)	−260.4(53)
O(17)	9 047.7(8)	7 896.0(23)	−204.1(30)
C(18)	8 811.6(12)	8 018.4(32)	−1 496.5(43)
C(19)	8 890.5(12)	8 977.2(31)	−2 284.4(40)
N(110)	8 892.5(12)	10 000	−1 485.6(45)
O(21)	3 445.9(13)	0	1 533.7(44)
C(22)	3 483(2)	956(4)	783(6)
C(23)	3 469(2)	1 917(5)	1 681(6)
O(24)	3 142.8(11)	1 985.6(40)	2 016.3(42)
C(25)	3 099(2)	2 952(6)	2 784(7)
C(26)	3 191(2)	2 885(5)	4 134(7)
O(27a)*	2 946(2)	2 069(5)	4 387(6)
O(27b)*	3 179(2)	1 881(7)	4 874(8)
C(28)	2 987(3)	1 859(5)	5 625(8)
C(29)	2 859(2)	943(4)	6 138(6)
N(210)	2 889(2)	0	5 420(5)
O(1)	9 542.6(12)	10 000	52.5(41)
C(001)*	851(4)	420(12)	7 192(13)
C(002)	1 071(2)	0	6 362(8)
N(001)	1 243(3)	0	5 685(8)

* Occupancy = 0.5.

Final refinement was on F by least-squares methods, including an extinction parameter [final value 0.000 43(3)]. Largest positive and negative peaks on a final Fourier difference synthesis were of height ± 0.7 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.002$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.038$, $R' = 0.062$, $S = 1.19$; R for all reflections = 0.045. Maximum shift/error in final cycle 0.10. Computing with SHELXTL PLUS on a DEC MicroVax-II computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from International Tables (1974) (stored in the program). Final atomic coordinates are given in Table 1, and selected bond lengths and angles in Table 2.

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

Results and Discussion

Equimolar addition of $SnCl_4$ and HL in acetonitrile provides the white compound $SnCl_3L$ with release of HCl. Analytical and spectroscopic data are consistent with partial encapsulation of a $SnCl_3$ unit involving terdentate chelation from the deprotonated nitrogen atom and the two adjacent oxygen atoms of the azacrown as depicted (Fig. 1).

The ^1H NMR spectrum of compound **1** contains three multiplets centred at δ 3.24, 3.63 and 3.68 corresponding to the $CH_2{}^a$, $CH_2{}^{c-f}$ and $CH_2{}^b$ protons respectively (relative intensity 1 : 4 : 1). Each signal is shifted downfield with respect to the free ligand, $CH_2{}^a$ (Δ 0.56), $CH_2{}^b$ (0.21) and $CH_2{}^{c-f}$ (0.14 ppm), in accord with the proposed metal chelation. The ^{13}C NMR spectrum corroborates this picture: the pure ligand shows a singlet CH_2NCH_2 (δ 50.61) and a five-line multiplet centred at

Table 2 Bond lengths (Å) and angles (°)

Sn(1)–Cl(11)	2.381(2)	Sn(1)–Cl(12)	2.371(2)
Sn(1)–Cl(13)	2.421(2)	Sn(1)–Cl(14)	2.397(2)
Sn(1)–O(15)	2.187(4)	Sn(1)–Cl(1a)	2.381(2)
Sn(2)–Cl(21)	2.398(2)	Sn(2)–Cl(22)	2.369(3)
Sn(2)–Cl(23)	2.356(3)	Sn(2)–Cl(24)	2.415(3)
Sn(2)–O(25)	2.234(4)	Sn(2)–Cl(2a)	2.398(2)
O(11)–C(12)	1.419(6)	O(11)–C(12a)	1.419(6)
C(12)–C(13)	1.485(8)	C(13)–O(14)	1.410(6)
O(14)–C(15)	1.421(6)	C(15)–C(16)	1.486(7)
C(16)–O(17)	1.431(6)	O(17)–C(18)	1.415(5)
C(18)–C(19)	1.490(6)	C(19)–N(110)	1.484(5)
N(110)–C(19a)	1.484(5)	O(21)–C(22)	1.418(6)
O(21)–C(22a)	1.418(6)	C(22)–C(23)	1.490(8)
C(23)–O(24)	1.431(8)	O(24)–C(25)	1.444(9)
C(25)–C(26)	1.315(9)	C(26)–O(27a)	1.465(11)
C(26)–O(27b)	1.441(10)	O(27a)–C(28)	1.238(10)
O(27b)–C(28)	1.201(14)	C(28)–C(29)	1.384(10)
C(29)–N(210)	1.381(6)	N(210)–C(29a)	1.381(6)
Cl(11)–Sn(1)–Cl(12)	90.8(1)	Cl(11)–Sn(1)–Cl(13)	91.2
Cl(12)–Sn(1)–Cl(13)	94.4(1)	Cl(11)–Sn(1)–Cl(14)	89.0(1)
Cl(12)–Sn(1)–Cl(14)	172.3(1)	Cl(13)–Sn(1)–Cl(14)	93.3(1)
Cl(11)–Sn(1)–O(15)	88.8	Cl(12)–Sn(1)–O(15)	84.9(1)
Cl(13)–Sn(1)–O(15)	179.4(1)	Cl(14)–Sn(1)–O(15)	87.3(1)
Cl(11)–Sn(1)–Cl(1a)	176.9(1)	Cl(12)–Sn(1)–Cl(1a)	90.8(1)
Cl(13)–Sn(1)–Cl(1a)	91.2	Cl(14)–Sn(1)–Cl(1a)	89.0(1)
O(15)–Sn(1)–Cl(1a)	88.8	Cl(21)–Sn(2)–Cl(22)	88.9(1)
Cl(21)–Sn(2)–Cl(23)	93.8	Cl(22)–Sn(2)–Cl(23)	100.5(1)
Cl(21)–Sn(2)–Cl(24)	90.1(1)	Cl(22)–Sn(2)–Cl(24)	164.9(1)
Cl(23)–Sn(2)–Cl(24)	94.6(1)	Cl(21)–Sn(2)–O(25)	86.3
Cl(22)–Sn(2)–O(25)	84.7(1)	Cl(23)–Sn(2)–O(25)	174.8(1)
Cl(24)–Sn(2)–O(25)	80.2(1)	Cl(21)–Sn(2)–Cl(2a)	172.4(1)
Cl(22)–Sn(2)–Cl(2a)	88.9(1)	Cl(23)–Sn(2)–Cl(2a)	93.8
Cl(24)–Sn(2)–Cl(2a)	90.1(1)	O(25)–Sn(2)–Cl(2a)	86.3
C(12)–O(11)–C(12a)	111.9(5)	O(11)–C(12)–C(13)	109.6(4)
C(12)–C(13)–O(14)	108.2(4)	C(13)–O(14)–C(15)	113.0(4)
O(14)–C(15)–C(16)	109.0(4)	C(15)–C(16)–O(17)	109.3(5)
C(16)–O(17)–C(18)	113.5(4)	O(17)–C(18)–C(19)	112.7(3)
C(18)–C(19)–N(110)	110.6(4)	C(19)–N(110)–C(19a)	114.9(4)
C(22)–O(21)–C(22a)	111.1(6)	O(21)–C(22)–C(23)	107.8(5)
C(22)–C(23)–O(24)	111.1(5)	C(23)–O(24)–C(25)	114.1(5)
O(24)–C(25)–C(26)	117.2(6)	C(25)–C(26)–O(27a)	100.9(6)
C(25)–C(26)–O(27b)	123.2(6)	C(26)–O(27a)–C(28)	112.4(6)
C(26)–O(27b)–C(28)	116.5(8)	O(27a)–C(28)–C(29)	124.7(6)
O(27b)–C(28)–C(29)	127.3(7)	C(28)–C(29)–N(210)	113.1(6)
C(29)–N(210)–C(29a)	113.3(6)		

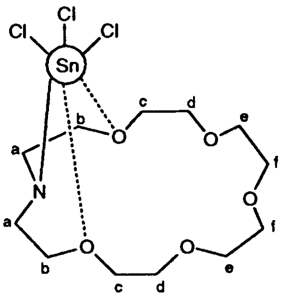

Fig. 1 Schematic representation of compound **1**

δ 71.18 for the remaining carbon sites. For **1** the C^a resonance has been shifted upfield by Δ 4.80 ppm, the C^b signal shows an even larger upfield shift of Δ 6.04 ppm whereas the remaining C^{c-f} multiplet is almost unchanged (Δ 0.64 ppm). The IR spectrum shows the characteristic ν_{asym}(C–O–C) stretching band shifted (Δ 22 cm^{-1}) to lower energy at 1088 cm^{-1} and an intense broad ν(Sn–Cl) stretching vibration at 321 cm^{-1}.

In an attempt to obtain crystals of diffraction quality, compound **1** was recrystallised from boiling acetonitrile. Colourless block crystals were obtained but this product, as confirmed by the crystal structure determination, turned out to be the unusual aquapentachlorostannate(IV) salt $[H_2L]_2[SnCl_5(H_2O)]_2·H_2O·MeCN$ **2**. Formation of this salt can be rationalised in terms of inadvertent partial hydrolysis of **1** resulting from trace water contamination of the solvent and/or an undetected deterioration of the in-house nitrogen supply. Nucleophilic (H_2O) attack at Sn^{IV} results in cleavage of Sn–Cl and Sn–N bonds with release of HCl and regeneration of the parent ligand HL respectively. The presence of aqueous HCl promotes protonation of HL to give the (ammonium) cation H_2L^+ and also allows nucleophilic attack (H_2O/Cl^-) on $SnCl_3(OH)$ intermediates leading to the formation of the aquapentachloro anion. The overall metal balance is preserved through the removal of some of the Sn^{IV} as insoluble polymeric 'oxo' species $[Sn(OH)(H_2O)O?]$.

The structure of compound **2** consists of two independent $[H_2L]^+$ cations, one of which is partly disordered, two $[SnCl_5(H_2O)]^-$ anions and a water molecule of hydration all of which are interlinked by an extensive hydrogen-bonding network. A further solvate molecule (MeCN) is located within the lattice. Perspective views showing the molecular geometries of the azacrown ligands and their associated water and $[SnCl_5(H_2O)]^-$ anions are shown in Figs. 2 and 3. The ordered cation (ring 1) lies on a crystallographic mirror plane. The uncoordinated water molecule is located above the cavity of this protonated azacrown ring with its oxygen atom forming

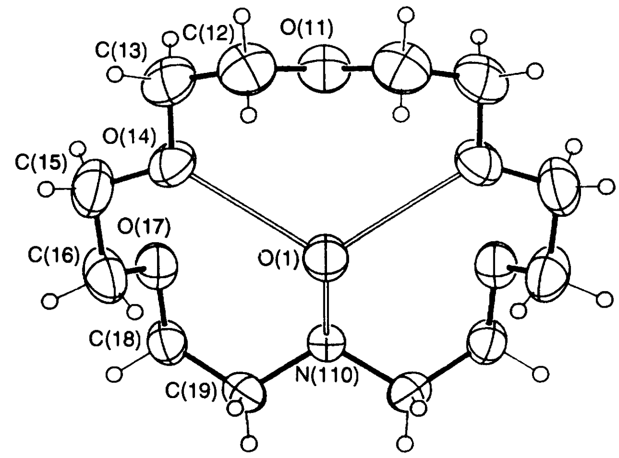

Fig. 2 The $[H_2L]^+·H_2O$ unit showing the atom numbering

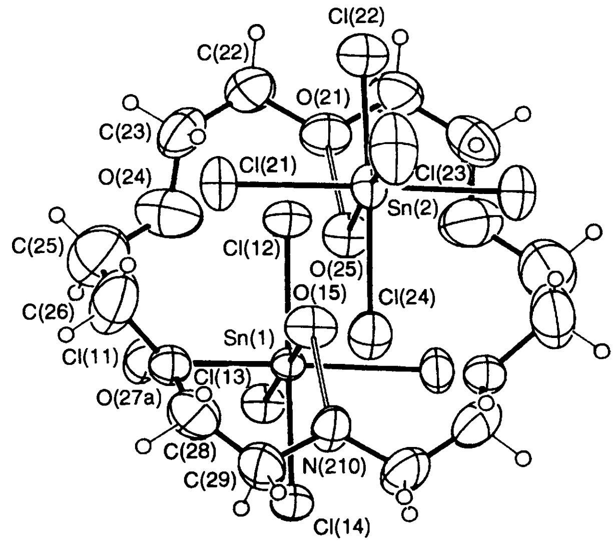

Fig. 3 The $[H_2L]^+·2[SnCl_5(H_2O)]^-$ unit showing the atom numbering. Only one of the alternative positions for O(27) is included

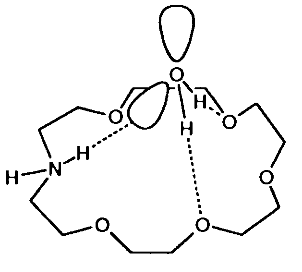

Fig. 4 Schematic representation of cavity hydrogen bonding associated with cation ring 1 in compound **2**

essentially equidistant hydrogen bonds with the nitrogen atom and two of the oxygen atoms, O(1)···O(14)/O(14a) 2.793 and O(1)···N(110) 2.690 Å. A least-squares plane through all six ring heteroatoms shows displacements of N(110), O(14), O(14a) (set A) of +0.31 Å and O(11)O(17)O(17a) (set B) of −0.31 Å. The oxygen atom of the water molecule lies 0.98 Å above the mean plane. This co-ordinated unit has been observed previously in the 'hydrated ammonium chloride complex' $[H_2L(H_2O)]Cl$ obtained by Gokel and Garcia[14] from direct treatment of HL with hydrochloric acid. Based on spectroscopic and crystal structure analyses the cation of this hydrochloride salt was identified as the monohydrate of the protonated (ammonium) form of the azacrown rather than a hydronium complex of the neutral ligand. The relevant separation distances are $O_{water}\cdots O_{ring}$ 2.898, 2.909 and $O_{water}\cdots N_{ring}$ 2.727 Å. A schematic representation of the geometry and cavity hydrogen bonding associated with the cation ring **1** is depicted in Fig. 4.

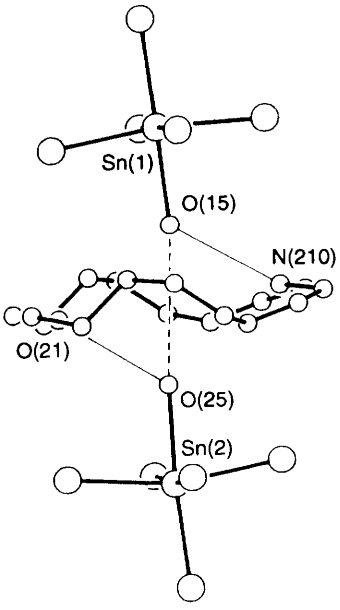

Fig. 5 Side view of the $[H_2L]^+\cdot 2[SnCl_5(H_2O)]^-$ unit showing the principal hydrogen bonds formed by O(15) and O(25) and the line joining these atoms to the centroid of the ring heteroatoms [omitting O(27a)]

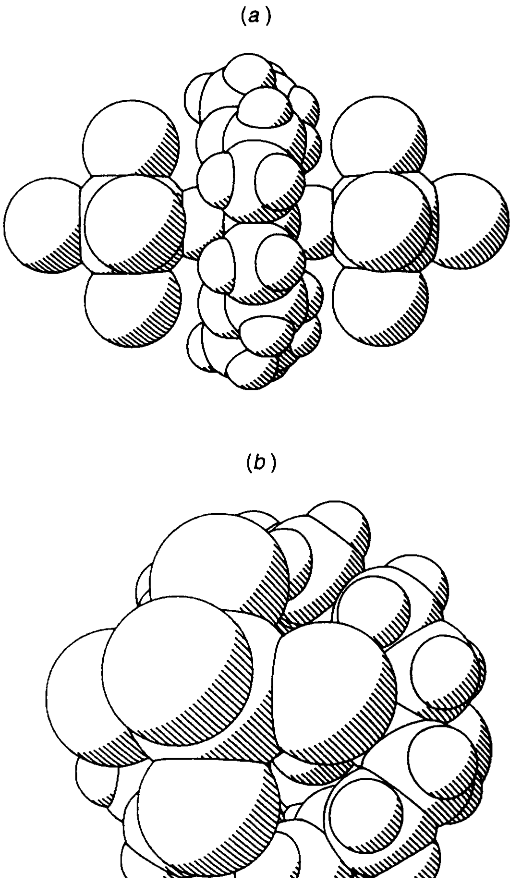

Fig. 6 Space-filling pictures of the $[H_2L]^+\cdot 2[SnCl_5(H_2O)]^-$ unit viewed (*a*) perpendicular to the O(15)···O(25) axis and (*b*) overlooking the ring cavity

The two six-co-ordinate $[SnCl_5(H_2O)]^-$ anions are located on opposite sides of the azacrown molecule 2 with the co-ordinated H_2O molecules positioned over the central cavity. There is slight distortion from octahedral geometry around the metal centres. For Sn(1) the Sn–Cl bond distances lie in the range 2.371(2)–2.421(2) Å (mean 2.393 Å) [the longest involves Cl(13) which is *trans* to the co-ordinated water molecule], the Sn–O bond distance is 2.187(4) Å and the interligand angles Cl–Sn–O (mean) 87.0°; the corresponding values for Sn(2) are Sn–Cl 2.356(3)–2.415(3) Å (mean 2.385 Å) [interestingly the longest bond distance here involves Cl(24) which is *cis* to the co-ordinated water molecule], Sn–O 2.234(4) Å, (mean) Cl–Sn–O 83.7°. This particular tin(IV) anion has been previously identified crystallographically in $[Mo(CO)_4\{Ph_2P(CH_2)_2PPh_2\}(SnCl_3)][SnCl_5(H_2O)]$[15] (mean) Sn–Cl 2.37, Sn–O 2.24 Å, $[Mo(\eta\text{-}C_5H_5)(CO)(NO)(PPh_3)(SnCl_3)][SnCl_5(H_2O)]$[16] (mean) Sn–Cl 2.38, Sn–O 2.24 Å and $[C_6H_{13}N_2][SnCl_5(H_2O)]\cdot H_2O$[17] ($C_6H_{13}N_2$ = 4,5-dihydro-3,5,5-trimethylpyrazolium) (mean) Sn–Cl 2.39, Sn–O 2.17 Å. The corresponding tetrahydrofuran (thf) (solvate) anion is also known, *e.g.* $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$,[18] *trans*- $[CrCl_2(thf)_4][SnCl_5(thf)]$[18] and *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$.[19] Each of the co-ordinated water molecules is involved in hydrogen bonding with the azacrown molecule 2. For this particular ring a least-squares plane taken through the ring heteroatoms but omitting O(27a)/O(27a′), which gives a more centrally placed plane than the alternative set, shows a fairly symmetrical puckering, O(21) and O(27b)/O(27b′) being to one side (+0.45 Å), and N(210) and O(24)/O(24′) to the other (−0.45 Å). The co-ordinated water molecules O(15) and O(25) are displaced −1.69 and +1.82 Å respectively from the plane. For Sn(1) the water oxygen atom O(15) participates in one short contact to the nitrogen atom of the ring, O(15)···N(210) 2.755 Å and makes contacts of 3.038 Å to O(24) and longer contacts of 3.099 Å to O(27a) and 3.239 Å to O(21). The water molecule co-ordinated to Sn(2) makes one short contact to one of the ring oxygen atoms, O(25)···O(21) 2.784 Å and a longer contact to O(27B) (2.989 Å). The separation between the two water molecules is O(15)···O(25) 3.52 Å and their relative positions with respect to the perpendicular axis passing through the ring

Table 3 Ligand torsion angles (°) (angles in the second half of each ring are the reverse of those listed)

Central bond	Ligand 1	Ligand 2*
O(1)–C(2)	−172.8	−176.5
C(2)–C(3)	67.2	−62.7
C(3)–O(4)	168.7	174.8
O(4)–C(5)	175.4	−90.6
C(5)–C(6)	−75.5	−64.3/−29.1
C(6)–O(7)	−175.9	179.1/−117.0
O(7)–C(8)	−88.0	−162.5/160.6
C(8)–C(9)	−58.2	41.6/−17.4
C(9)–N(10)	−166.9	161.9

* Alternative values relate to O(27a) and O(27b).

centroid is shown in projection in Fig. 5. The lines joining O(15) and O(25) to the centroid of the heteroatoms [omitting O(27a)] are almost collinear and make angles of 1.6 and 0.7° with the normal to the ring plane. However the Sn–O directions are not quite in line with the O(15)···O(25) axis; each $SnCl_5$ unit is tilted away from the particular ring segment through which it forms its principal hydrogen-bond interaction, see Figs. 5 and 6. Clearly the azacrown cation (ring 2) acts as a second-sphere ligand to the $[SnCl_5(H_2O)]^-$ units in much the same manner as has been found for the homoleptic oxacrown 18-crown-6 with the neutral $SnCl_4(H_2O)_2$ and $SnMe_2Cl_2(H_2O)$ units.[2–4]

The two crystallographically independent azacrown molecules adopt dissimilar ring conformations. Torsion angles are listed in Table 3. Ring 1 is mirror-symmetric with essentially invariant C–C (mean) 1.487 and C–O (mean) 1.419 Å bond distances, *cf.* $[Pb(HL)][NO_3]_2$ [C–C (mean) 1.504, C–O (mean) 1.417 Å] where the lead(II) cation lies in the cavity of the neutral macrocycle.[20] Torsion angles around the C–C bonds lie in the range 58.2–75.5° (mean 66.9°) reflecting a *gauche* (60°) conformation. For the C–O bonds eight of the ten torsion angles have values within ±4° of their mean value of 173.2°. With torsion angles of 166.9° around the two C–N bonds the sole 'exception' to a symmetrical *anti* (180°) pattern for the whole ring comes from the remaining two O(7)–C(8) bonds with torsion angles of 88.0°, *i.e.* a skew conformation (90°). Nevertheless a relatively strain-free ring structure is present. However with ring 2 the pattern of bond distances and torsion angles is confused by the disorder at O(27). Using the values observed for ring 1 as reference it is clear that this azacrown molecule also shows a significant difference at O(24) which has a skew bond to C(25).

Acknowledgements

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