# Stereochemical Activity of Lone Pairs. The Crystal and Molecular Structures of the Salts of Chloro(1,4,7,10,13,16-hexaoxacyclo-octadecane)tin(II).* Calculation of Macrocyclic Cavity Size by Force Field Methods

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The crystal structures of the trichlorostannate(II), (**1**), and perchlorate, (**2**), salts of chloro-(1,4,7,10,13,16-hexaoxacyclo-octadecane)tin(II), $[Sn(18\text{-crown-}6)Cl]^+$, have been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals of both complexes are triclinic, space group $P\bar{1}$, with $Z = 2$ and 4, in unit cells of dimensions $a = 12.049(8)$, $b = 7.733(8)$, $c = 12.717(9)$ Å, $\alpha = 107.0(1)$, $\beta = 82.1(1)$, $\gamma = 89.0(1)°$ and $a = 8.053(8)$, $b = 23.964(15)$, $c = 11.747(8)$ Å, $\alpha = 92.6(1)$, $\beta = 118.8(1)$, $\gamma = 88.3(1)°$, respectively. The structures were refined to $R = 0.073$ and 0.088 for 2 991 and 4 032 observed reflections respectively. Both complexes contain $[Sn(18\text{-crown-}6)Cl]^+$ in which the tin occupies a hexagonal pyramidal site being bonded to all six crown oxygens [Sn–O 2.592(6)—2.883(7) Å] and a chlorine atom [Sn–Cl 2.428(2) Å] in an axial position. Structure (**2**) contains two independent sets of these complex cations. The tin lone pair exhibits much reduced stereochemical activity and this behaviour is discussed on the basis of the structures and the Mössbauer parameters. Molecular mechanics calculations of hole size show that the best fit for a metal within 18-crown-6 in the $D_{3d}$ conformation is provided by M–O bond lengths of 2.85 Å.

The unusual properties of macrocyclic polyethers[1] have been shown to extend to complexes with a number of tin(II) acceptors.[2,3] Complexes formed between 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5, $L^1$) or 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6, $L^2$) and tin(II) chloride or tin(II) thiocyanate have been interpreted on the basis of the formulations $[Sn(L^1)_2][SnX_3]_2$ and $[Sn(L^2)X][SnX_3]$, where X = Cl or NCS.[2,3] The recent crystal structure determination[4] of the 15-crown-5 complex with tin(II) chloride corroborates the first formulation and is consistent with the lone pair on the complexed tin cation being sterically inactive. Until this result, all previous crystallographic studies on tin(II) acceptor complexes with *neutral* ligands had shown that the tin atoms are sited in distorted environments. These distortions are generally satisfactorily rationalised by the valence shell electron pair repulsion (v.s.e.p.r.) model when a sterically active tin lone pair is invoked.[5] Contrasting with the Mössbauer data for the 15-crown-5 systems, the chemical shifts and quadrupole splittings for the 18-crown-6 complexes, with one exception, are typical of non-cubic tin(II) environments,[3] *i.e.* the presence of a stereochemically active lone pair. The exception is the tin(II) perchlorate complex which, in the absence of reliable elemental analyses, appears to resemble the 15-crown-5 systems as far as Mössbauer parameters are concerned.

We report here the crystal structures of chloro(18-crown-6)-tin(II) trichlorostannate(II) and of a new complex, chloro-(18-crown-6)tin(II) perchlorate.

## Experimental

*Preparation.*—There are two routes for preparing tin(II) acceptor–crown ether complexes. The first is that reported by Herber *et al.*[2,3] in which non-aqueous solvents are used and the second is that described by Hough *et al.*[4] where reaction takes place in acidic solutions. The following reactions were carried out in the absence of oxygen.

(*a*) Chloro(18-crown-6)tin(II) trichlorostannate(II), $[Sn(L^2)Cl][SnCl_3]$ (**1**), was prepared by modifying the first method. 18-Crown-6 (2.6 g) in methanol (10 $cm^3$) was added to tin(II) chloride dihydrate (2.1 g) in methanol (30 $cm^3$) acidified by adding hydrochloric acid (5 mol $dm^{-3}$, 4 drops). Diffraction quality crystals were formed after several hours at 5 °C.

(*b*) Chloro(18-crown-6)tin(II) perchlorate, $[Sn(L^2)Cl][ClO_4]$ (**2**), reported for the first time here, was prepared by the second route. Tin(II) dichloride dihydrate (2.1 g) in perchloric acid (9 mol $dm^{-3}$, 10 $cm^3$) and water (5 $cm^3$) was added to 18-crown-6 (2.6 g) in water (5 $cm^3$). The crystals, which were obtained after 1 h were recrystallised from methanol.

*Crystal Data for* $[Sn(L^2)Cl][SnCl_3]$ (**1**).—$C_{12}H_{24}Cl_4O_6Sn_2$, $M = 643.4$, triclinic, $a = 12.049(8)$, $b = 7.733(8)$, $c = 12.717(9)$ Å, $\alpha = 107.0(1)$, $\beta = 82.1(1)$, $\gamma = 89.0(1)°$, $U = 1\,120.6$ Å$^3$, $Z = 2$, $F(000) = 624$, $D_m = 1.87$ g $cm^{-3}$, $D_c = 1.91$ g $cm^{-3}$, $\lambda = 0.7107$ Å, $\mu = 27.33$ $cm^{-1}$. No absent spectra; possible space groups $P1$ or $P\bar{1}$; $P\bar{1}$ from structure analysis.

*Crystal Data for* $[Sn(L^2)Cl][ClO_4]$ (**2**).—$C_{12}H_{24}Cl_2O_{10}Sn$, $M = 373.6$, triclinic, $a = 8.053(8)$, $b = 23.964(15)$, $c = 11.747(8)$ Å, $\alpha = 92.6(1)$, $\beta = 118.8(1)$, $\gamma = 88.3(1)°$, $U = 1\,984.5$ Å$^3$, $Z = 4$, $F(000) = 1\,040$, $D_m = 1.73$ g $cm^{-3}$, $D_c = 1.72$ g $cm^{-3}$, $\lambda = 0.7107$ Å, $\mu = 16.1$ $cm^{-1}$. No absent spectra; possible space groups $P1$ or $P\bar{1}$; $P\bar{1}$ from structure analysis.

*Intensity Data Collection and Structure Refinement.*—Precession photographs established the preliminary cell parameters and space groups. Crystals were mounted to rotate about the *a* axes on a Stoe STADI2 diffractometer and data were collected *via* a variable-width scan. Background counts were 20 s and a scan rate of 0.0333° $s^{-1}$ was applied to a width of (2.0 + 0.5 $\sin\mu/\tan\theta$). Intensity data were collected out to $2\theta < 50°$.

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* *Supplementary data available* (No. SUP 56499, 11 pp.): H-atom co-ordinates, thermal parameters, torsion angles, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

*Non-S.I. units employed*: dyn = $10^{-5}$ N, cal = 4.184 J.

**Table 1.** Atomic co-ordinates ( × $10^4$) for (**1**) with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Sn(1) | 2 135(0) | 1 313(1) | 2 221(0) | O(7) | 4 476(6) | 1 472(9) | 2 214(6) |
| Sn(2) | 3 350(1) | 1 795(1) | 5 501(1) | C(8) | 5 255(8) | 20(14) | 1 534(10) |
| Cl(1) | 2 248(2) | 2 124(3) | 505(2) | C(9) | 4 706(10) | −1 682(16) | 1 418(10) |
| Cl(2) | 1 432(3) | 1 030(5) | 5 052(3) | O(10) | 3 713(6) | −1 630(8) | 927(6) |
| Cl(3) | 3 680(3) | −1 128(5) | 5 854(3) | C(11) | 3 244(10) | −3 367(12) | 580(10) |
| Cl(4) | 2 784(3) | 3 463(4) | 7 499(3) | C(12) | 2 165(10) | −3 107(13) | 187(9) |
| O(1) | 804(6) | 4 155(9) | 3 228(7) | O(13) | 1 403(6) | −1 989(9) | 1 114(6) |
| C(2) | 1 240(12) | 5 887(14) | 3 355(13) | C(14) | 279(10) | −1 944(15) | 876(11) |
| C(3) | 2 325(13) | 5 867(15) | 3 772(13) | C(15) | −443(10) | −729(16) | 1 833(12) |
| O(4) | 3 066(7) | 4 531(9) | 2 969(6) | O(16) | −33(6) | 3 014(10) | 2 071(7) |
| C(5) | 4 186(10) | 4 555(16) | 3 222(11) | C(17) | −752(11) | 2 369(19) | 2 922(16) |
| C(6) | 4 907(10) | 3 201(15) | 2 336(11) | C(18) | −312(11) | 4 154(17) | 2 936(17) |

**Table 2.** Atomic co-ordinates ( × $10^4$) for (**2**) with estimated standard deviations in parentheses

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Sn(1) | 1 788(1) | 1 266(0) | 2 483(1) | Sn(2) | 1 812(1) | 6 237(0) | 2 639(1) |
| Cl(3) | 1 858(6) | 1 160(2) | 423(4) | Cl(2) | 2 311(5) | 5 293(2) | 6 119(4) |
| Cl(1) | 2 271(7) | 1 260(2) | 5 987(5) | Cl(4) | 1 936(6) | 6 211(2) | 604(4) |
| O(11) | 1 220(23) | 1 746(5) | 5 443(18) | O(21) | 3 952(18) | 5 294(6) | 5 922(19) |
| O(12) | 1 168(23) | 788(6) | 5 389(22) | O(22) | 1 397(19) | 5 808(5) | 5 400(16) |
| O(13) | 3 825(26) | 1 246(7) | 5 741(19) | O(23) | 1 278(18) | 6 774(5) | 5 579(18) |
| O(14) | 3 087(59) | 1 241(13) | 7 215(23) | O(24) | 2 950(35) | 6 272(9) | 7 452(20) |
| O(1A) | 4 107(19) | 2 116(5) | 3 110(13) | O(1B) | 2 006(16) | 7 357(4) | 2 755(10) |
| C(2A) | 3 374(56) | 2 573(11) | 2 313(27) | C(2B) | 3 777(26) | 7 564(7) | 2 960(17) |
| C(3A) | 1 685(63) | 2 742(11) | 2 018(30) | C(3B) | 5 315(21) | 7 253(7) | 3 903(18) |
| O(4A) | 352(21) | 2 308(6) | 1 543(13) | O(4B) | 5 131(14) | 6 687(4) | 3 522(10) |
| C(5A) | −1 590(44) | 2 419(9) | 1 259(26) | C(5B) | 6 757(18) | 6 368(7) | 4 414(14) |
| C(6A) | −2 638(37) | 1 938(17) | 569(34) | C(6B) | 6 510(19) | 5 826(7) | 3 766(19) |
| O(7A) | −2 230(20) | 1 478(7) | 1 204(16) | O(7B) | 4 817(13) | 5 582(4) | 3 548(9) |
| C(8A) | −3 424(26) | 1 017(16) | 356(29) | C(8B) | 4 598(22) | 5 017(6) | 3 021(16) |
| C(9A) | −2 641(68) | 555(20) | 1 198(40) | O(9B) | 2 911(21) | 4 793(6) | 3 003(17) |
| O(10A) | −924(26) | 426(7) | 1 471(18) | O(10B) | 1 302(14) | 5 120(4) | 2 229(9) |
| C(11A) | −375(45) | −73(10) | 2 158(33) | C(11B) | −461(27) | 4 931(7) | 2 084(16) |
| C(12A) | 1 306(57) | −212(10) | 2 156(32) | C(12B) | −1 959(21) | 5 189(6) | 1 038(17) |
| O(13A) | 2 828(22) | 215(5) | 2 926(14) | O(13B) | −1 833(14) | 5 773(4) | 1 351(10) |
| C(14A) | 4 373(54) | 76(10) | 2 967(37) | C(14B) | −3 231(25) | 6 082(8) | 324(18) |
| C(15A) | 5 834(28) | 440(11) | 3 940(24) | C(15B) | −3 365(19) | 6 641(8) | 801(19) |
| O(16A) | 5 315(15) | 1 006(5) | 3 474(11) | O(16B) | −1 526(13) | 6 898(5) | 1 246(11) |
| C(17A) | 6 455(33) | 1 428(13) | 4 249(26) | C(17B) | −1 419(28) | 7 446(8) | 1 844(19) |
| C(18A) | 6 116(37) | 1 938(13) | 3 476(30) | C(18B) | 378(23) | 7 717(7) | 1 938(18) |

For both intensity data sets reflections were classified as observed by the condition $I_{net} > 3\sigma(I)$. Thus for (**1**), of the 3 810 independent reflections measured, 2 991 were classified as observed; the corresponding figures for (**2**) are 7 331 and 4 032 respectively.

Data were corrected for Lorentz and polarisation effects. Scattering factors and dispersion corrections were taken from ref. 6. Solutions and refinements were carried out by using the SHELX 76 package[7] and plots were drawn by the program ORTEP.[8]

Both structures were solved from the Patterson function and subsequent Fourier syntheses in space group $P\bar{1}$. Whereas structure (**1**) was straightforward, structure (**2**) was complicated by containing two independent sets of cations and anions with the related co-ordinates ($x,y,z$; $x,\frac{1}{2} + y,z$). These two sets were successfully disentangled. In both structures the Sn, Cl, O, and C atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. In (**1**) hydrogen atoms bonded to a common carbon atom were given the same refined thermal parameter; in (**2**) hydrogen atoms in the same ligand were given a common refined thermal parameter. The structures were refined by full-matrix least squares to $R$ values of 0.073 ($R'$ 0.072) and 0.088 ($R'$ 0.105) respectively. The weighting scheme,

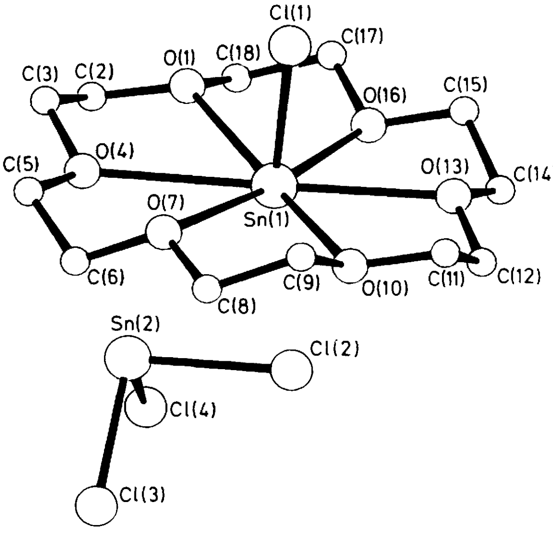

Figure 1. The structure of $[Sn(L^2)Cl][SnCl_3]$, together with the atomic numbering scheme

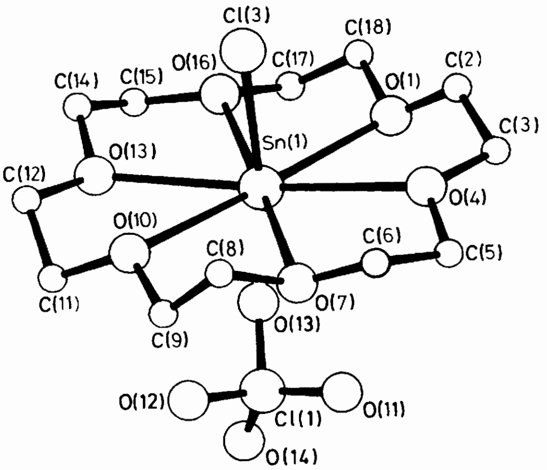

**Figure 2.** The structure of $[Sn(L^2)Cl][ClO_4]$. Molecule **A** is shown together with the atomic numbering scheme. Molecule **B** has an equivalent geometry

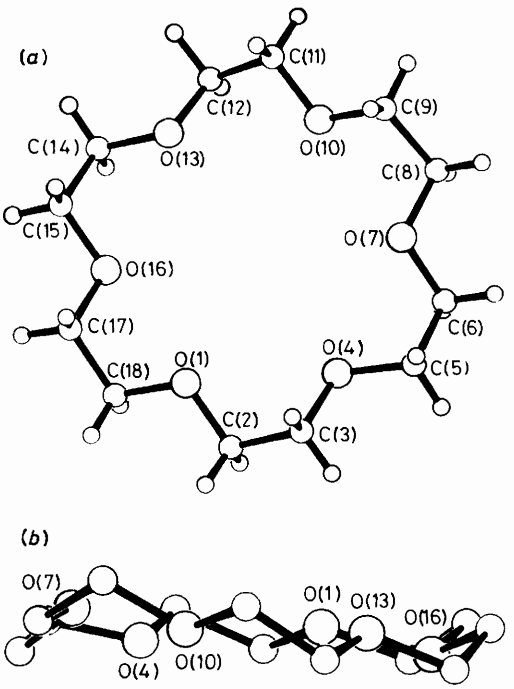

**Figure 3.** (*a*) The crown ether ligand viewed in the direction normal to its mean plane; (*b*) view along a direction in the mean plane (hydrogen atoms omitted)

$w = 1/[\sigma^2(F) + 0.003F^2]$, was chosen to give similar values of $w\Delta^2$ over ranges of $F_o$ and sin $\theta/\lambda$. The atomic positions are given in Tables 1 and 2 and interatomic distances and valence angles in Tables 3 and 4.

## Results and Discussion

The crystal structures consist of complex $[Sn(L^2)Cl]^+$ cations and for (**1**) $[SnCl_3]^-$ or (**2**) $[ClO_4]^-$ anions. This confirms the formulation suggested for (**1**) by Herber and Smelkinson[2] in their interpretation of the Mössbauer spectrum. The $[Sn(L^2)Cl]^+$ cation in (**1**), and that for (**2**) (see below), are shown in Figures 1 and 2 together with the atom numbering scheme. In the case of (**2**) there are two independent cations (designated **A** and **B**) of identical stoicheiometry and similar geometry. All three cations (**1**), (**2A**), and (**2B**) have similar structures as shown by the bond parameters (Tables 3 and 4), torsion angles, and the least-squares planes. As shown by the estimated standard deviations, the bond parameters derived for structure (**1**) are more accurately determined than those in (**2**). The C–C and C–O bond distances in (**1**) and (**2**) are comparable, within the standard deviations, with those reported for other cyclic polyethers.[9–11] The conformation of the crown ether, shown in Figure 3, may be idealised to $D_{3d}$ point symmetry.

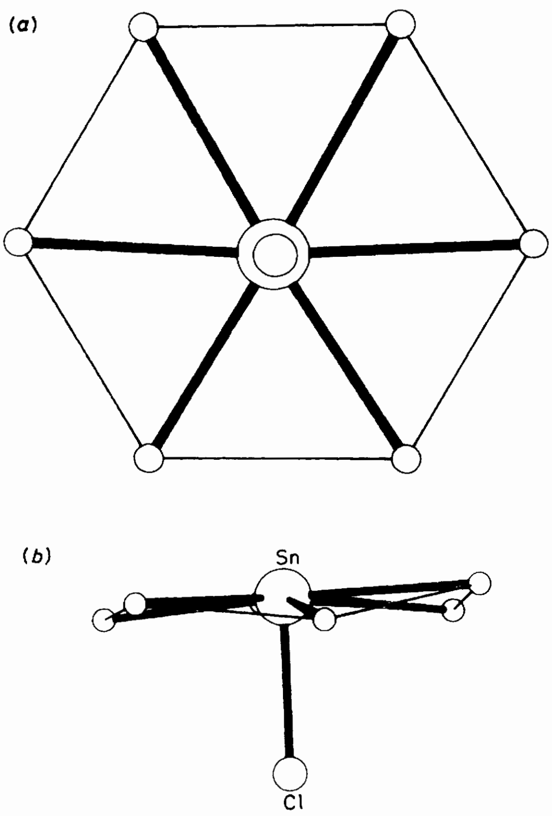

**Figure 4.** The immediate environment of the tin atom in $[Sn(L^2)Cl]^+$ (hydrogen atoms omitted): (*a*) view in the direction normal to the mean $O_6$ plane; (*b*) view in a direction within the mean $O_6$ plane

*Tin Co-ordination.*—As is the case for cations (**2A**) and (**2B**), in (**1**) tin is bonded to all six oxygen atoms of the crown, with bond lengths ranging from 2.592(6) to 2.883(7) Å. The immediate tin environment, shown in Figure 4, is best described as a hexagonal pyramid, or, if the lone pair is included at the remaining axial position, hexagonal bipyramid. Thus, the base of the pyramid consists of the $SnO_6$ group of atoms which form an approximate plane, the ring atoms deviating consecutively ±0.14 [average in (**1**)], ±0.13, ±0.15 Å [in (**2A**) and (**2B**), respectively]. The tin atom is sited 0.13 [in (**1**)], 0.14, 0.15 Å [in (**2A**) and (**2B**), respectively] below the $O_6$ plane on the opposite side to the axial chlorine atom. The symmetry of the $O_6$ group is close to $D_{3d}$. The Sn–Cl distance [2.428(2) Å] is somewhat shorter than those in the 1,4-dioxane adduct [2.474(2) Å]. Although apparently minor, this shortening does reveal a significantly stronger bond relative to the latter. An internal measure of normal, pyramidal, Sn–Cl bonds is the average value [2.481(4) Å] for the $[SnCl_3]^-$ anion.

**Table 3.** Molecular dimensions [distances (Å), angles (°)] in the tin co-ordination sphere of (**1**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sn(1)-Cl(1) | 2.428(2) | Sn(1)-O(7) | 2.823(7) | Sn(1)-O(16) | 2.654(7) | Sn(2)-Cl(3) | 2.466(4) |
| Sn(1)-O(1) | 2.592(6) | Sn(1)-O(10) | 2.883(7) | Sn(2)-Cl(2) | 2.495(4) | Sn(2)-Cl(4) | 2.483(4) |
| Sn(1)-O(4) | 2.713(7) | Sn(1)-O(13) | 2.756(6) | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Cl(1)-Sn(1)-O(4) | 83.45(18) | O(7)-Sn(1)-O(13) | 116.02(20) | O(4)-Sn(1)-O(1) | 61.93(23) |
| Cl(1)-Sn(1)-O(7) | 92.08(16) | O(10)-Sn(1)-O(13) | 59.19(20) | O(7)-Sn(1)-O(1) | 120.43(22) |
| O(4)-Sn(1)-O(7) | 59.21(21) | Cl(1)-Sn(1)-O(16) | 85.09(19) | O(10)-Sn(1)-O(1) | 173.51(22) |
| Cl(1)-Sn(1)-O(10) | 84.34(16) | O(4)-Sn(1)-O(16) | 123.44(23) | O(13)-Sn(1)-O(1) | 123.55(22) |
| O(4)-Sn(1)-O(10) | 114.44(21) | O(7)-Sn(1)-O(16) | 175.74(23) | O(16)-Sn(1)-O(1) | 62.84(24) |
| O(7)-Sn(1)-O(10) | 57.22(20) | O(10)-Sn(1)-O(16) | 119.20(22) | Cl(2)-Sn(2)-Cl(3) | 92.10(13) |
| Cl(1)-Sn(1)-O(13) | 88.26(16) | O(13)-Sn(1)-O(16) | 60.79(22) | Cl(2)-Sn(2)-Cl(4) | 97.23(12) |
| O(4)-Sn(1)-O(13) | 170.15(22) | Cl(1)-Sn(1)-O(1) | 89.80(19) | Cl(3)-Sn(2)-Cl(4) | 93.80(13) |

**Table 4.** Molecular dimensions [bond lengths (Å), bond angles (°)] in the tin co-ordination sphere of (**2**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sn(1)-Cl(3) | 2.450(5) | Sn(1)-O(10A) | 2.789(18) | Sn(2)-Cl(4) | 2.438(5) | Sn(2)-O(10B) | 2.706(9) |
| Sn(1)-O(1A) | 2.635(13) | Sn(1)-O(13B) | 2.626(12) | Sn(2)-O(1B) | 2.686(9) | Sn(2)-O(13B) | 2.811(10) |
| Sn(1)-O(4A) | 2.765(13) | Sn(1)-O(16A) | 2.567(11) | Sn(2)-O(4B) | 2.604(11) | Sn(2)-O(16B) | 2.856(9) |
| Sn(1)-O(7A) | 2.876(15) | | | Sn(2)-O(7B) | 2.627(9) | | |

| | | | | | |
|---|---|---|---|---|---|
| Cl(3)-Sn(1)-O(4A) | 82.10(38) | O(13B)-Sn(1)-O(16A) | 60.74(45) | O(4B)-Sn(2)-O(13B) | 172.29(39) |
| Cl(3)-Sn(1)-O(7A) | 92.77(41) | Cl(3)-Sn(1)-O(1A) | 88.35(38) | O(7B)-Sn(2)-O(13B) | 120.05(29) |
| O(4A)-Sn(1)-O(7A) | 59.38(48) | O(4A)-Sn(1)-O(1A) | 60.34(39) | O(10B)-Sn(2)-O(13B) | 58.57(30) |
| Cl(3)-Sn(1)-O(10A) | 85.6(5) | O(7A)-Sn(1)-O(1A) | 118.88(44) | Cl(4)-Sn(2)-O(16B) | 84.20(30) |
| O(4A)-Sn(1)-O(10A) | 113.49(44) | O(10A)-Sn(1)-O(1A) | 171.96(48) | O(4B)-Sn(2)-O(16B) | 119.64(32) |
| O(7A)-Sn(1)-O(10A) | 56.3(5) | O(13B)-Sn(1)-O(1A) | 125.34(45) | O(7B)-Sn(2)-O(16B) | 170.74(37) |
| Cl(3)-Sn(1)-O(13B) | 89.02(42) | O(16A)-Sn(1)-O(1A) | 64.72(38) | O(10B)-Sn(2)-O(16B) | 115.01(29) |
| O(4A)-Sn(1)-O(13B) | 169.47(41) | Cl(4)-Sn(2)-O(4B) | 82.14(30) | O(13B)-Sn(2)-O(16B) | 57.55(30) |
| O(7A)-Sn(1)-O(13B) | 115.77(49) | Cl(4)-Sn(2)-O(7B) | 86.91(29) | Cl(4)-Sn(2)-O(1B) | 90.02(30) |
| O(10A)-Sn(1)-O(13B) | 59.86(48) | O(4B)-Sn(2)-O(7B) | 61.40(31) | O(4B)-Sn(2)-O(1B) | 61.99(34) |
| Cl(3)-Sn(1)-O(16A) | 83.57(32) | Cl(4)-Sn(2)-O(10B) | 85.43(28) | O(7B)-Sn(2)-O(1B) | 123.19(32) |
| O(4A)-Sn(1)-O(16A) | 123.32(44) | O(4B)-Sn(2)-O(10B) | 121.98(33) | O(10B)-Sn(2)-O(1B) | 173.32(26) |
| O(7A)-Sn(1)-O(16A) | 174.88(43) | O(7B)-Sn(2)-O(10B) | 61.51(29) | O(13B)-Sn(2)-O(1B) | 116.68(32) |
| O(10A)-Sn(1)-O(16A) | 119.62(46) | Cl(4)-Sn(2)-O(13B) | 90.33(29) | O(16B)-Sn(2)-O(1B) | 59.53(30) |

*Some Considerations on Lone Pair Stereochemical Properties.*—In order to analyse the stereochemical implications of the lone pair in these structures and to place them in perspective with other complexes we present the background for the model used here.

Generally, lone pair steric activity, or inactivity, is deduced from geometrical information about a given atomic site, *i.e.* irregular co-ordinations are usually considered to stem largely from stereochemically active lone pairs. These are identified with apparent empty volumes within co-ordination polyhedra. More often than not, a localised, directed lone pair enables stereochemistries to be rationalised by means of the v.s.e.p.r. model. Thus, normal environments (*i.e.* in the absence of special constraints) for tin(II) in its compounds are trigonal pyramidal and distorted trigonal bipyramidal, the lone pair being placed at the apical ($SnX_3$ systems) and equatorial positions ($SnX_4$ systems) (X = any ligand), respectively.[12] In these cases the influence of the lone pairs is self evident. Identifying and characterising the properties of lone pairs is a complex problem. In most cases the stereochemical activities of lone pairs on central atoms can be explicitly expressed as a number of symmetry orbitals.[12–14] The physical foundation of the v.s.e.p.r. model has been attributed to the Pauli Exclusion Principle which forces electron pairs to occupy different regions of space. However, this assumption has been questioned.[15] A more realistic picture would appear to be more complicated. For example, on the basis of extended Hückel Theory, Hall[16,17] suggests that Pauli repulsions in covalent molecules are important only for those between bonds and that stereochemical activity results, not *primarily* from Pauli forces, but from a system's desire to lower its total energy through maximum population of the lower valence *s* orbital. This end is achieved through distortions appropriate in the context of the other energies relevant to the system as a whole.

For fifth-row elements such as tin, the larger sizes of the lower valent central atoms reduce the importance of Pauli repulsions. Contributions from both the *s* and *p* orbitals are responsible for stereochemical activity in the v.s.e.p.r. sense. A lone pair with pure *s* character has essentially antibonding character[4] since the symmetry of *s* orbitals always permits interaction with ligand group orbitals for all point groups. Such a lone pair is generally designated non-stereochemically active, a description in the v.s.e.p.r. sense. Yet, in a broader sense, this lone pair is active because it is the cause of long bonds, and because it is the result of the system being permitted to adjust its geometry so that the energy is reduced by optimum population of the *s* orbital. On the other hand, a lone pair with pure *p* character is better described as non-stereochemically active because it *must* have non-bonding character. Such lone pairs are relatively uncommon and can only arise in company with other lone pairs on a central atom and when the system adopts a point group (consistent with optimum population of the *s* orbital which relates to another lone pair) in which the symmetry of the *p* orbital is unique. Examples are the $b_1$ ($p_x$) orbitals in the $C_{2v}$ $H_2X$ gas molecules (X = O, S, Se, or Te). Strictly, this non-bonding lone pair also has some influence because the energies of non-bonding levels are influenced by variations in delocalisation into bonding and antibonding levels and thereby make some varying contributions to the energy. It is the admixture of *p*-type wavefunctions with the *s* wavefunction which introduces directional characteristics and hence influences bond angles. This background to the concept of the lone pair provides the basis for our examination of the stereochemical effects in compounds of lower valent main-group elements.[12–14]

Specifically, in the case of the present tin complexes the structures of dichloro(1,4-dioxane)tin(II), (**3**), which consists of $SnCl_2$ units linked by dioxane ligands to form polymeric arrays,[12] and monomeric bis(1-phenylbutane-1,3-dionato)-tin(II), (**4**),[18] are used for comparison. In both structures, the tin geometry is a distorted trigonal bipyramid with the active lone pair in an equatorial site. In these structures, according to the above description, the 5*s* contributions to levels defining the lone pair decrease with distortion of the axial O–Sn–O angle from 180°. The O–Sn–O angle in (**3**) is 169°. Evidently the normally dominating effects of the tin lone pair (v.s.e.p.r. sense) and its tendency to repel the oxygen atom are opposed by the constraining role of dioxane as a link between $SnCl_2$ units. The Sn–O bonds [2.527(5) Å] are some 0.2 Å longer than that in tin(II) chloride dihydrate[19] in which the water ligand imposes no extra constraint, and is therefore included here as an example of an unconstrained Sn–O bond length. Complex (**4**) exhibits the same co-ordination number and point symmetry as the dioxane adduct and, consisting of discrete molecules, the constraint here is not due to a polymeric effect but to the chelating properties of the ligand. Accordingly, there is a much larger deviation (30°) of the O–Sn–O axial angle from linearity and hence much shorter bonds [2.290(6) Å]. In both complexes there is a similar distortion of the equatorial angle from 120 to *ca.* 90°.

In common with (**3**) the steric influence of the tin lone pair (which is evidently directed along the remaining axial position) in the $[Sn(L^2)Cl]^+$ structure is effectively opposed by the steric effect of the axial chlorine atom. This time, however, the collective complexing requirements of the six oxygen atoms of the crown ether define these constraints. Thus, the $D_{3d}$ conformation of the crown ether would need to be more distorted for the Cl–Sn–O angles to be regularly less than 90° which is the usual expression of lone pair steric activity. An example of a complex with a similar hexagonal pyramidal structure is the lead(II) complex $[PbL^3(H_2O)]^{2+}$ of a hexa-aza analogue ($L^3$) of [18]annulene in which lead is bonded equatorially to six nitrogen atoms of the macrocycle and to the oxygen atom of a water molecule in one axial position of a distorted hexagonal pyramid.[20] In this case all six $N_{eq}$–Pb–$O_{ax}$ angles are less than 85° which is consonant with the lone pair in the remaining axial position (of the bipyramid) exerting a larger steric effect than in (**1**) and (**2**). Similar degrees of distortions in (**1**) and (**2**) would increase the strain energy of the crown and the repulsive energy of the chlorine interaction.

In this context, the structure[21] of $[CsL^2]^+$ is relevant because the cesium ion is evidently too large to fit into the cavity as defined by the $D_{3d}$ conformation and is therefore located 1.44 Å above the $O_6$ plane. It is evident from the present structures that tin(II) is not too large for this cavity, although the enhanced 5*s* character of the lone pair (see below) would be associated with an increase in size relative to tin(II) in most of its compounds. Nevertheless, given the constraints of the crown ether and the chlorine atom, evidence of lone pair steric activity, albeit strongly reduced, is provided by the small but significant displacement [0.14 Å mean for (**1**), (**2A**), and (**2B**)] of tin(II) from the mean $O_6$ plane in the direction of the lone pair. The comparable value in $[PbL^3(H_2O)]^{2+}$ is 0.48 Å.[20] As observed in the dioxane structure, repulsive forces between Sn–O bonding electrons and the tin lone pair can also be relieved by lengthening the Sn–O bonds. This is complicated in the present structures by the constraints of the crown ether. As is shown below, the ideal M–O distance for metal (M) complexes of a $D_{3d}$ crown ether is 2.85 Å. The $Na^+$ cation is considerably smaller than tin(II) and in order to accommodate this cation the crown adopts a different conformation in some $[Na(18\text{-crown-}6)]^+$ structures.[22–24] Even so, there are several structures of $[Na(18\text{-crown-}6)]^+$ with the crown in the $D_{3d}$ conformation.[24–27] In many of these complexes the $Na^+$ ion is displaced to one end of the 18-crown-6 thereby forming short and long contacts (2.67—2.79,[24] 2.62—2.96,[25] 2.73—2.85,[26] 2.65—2.95 Å[27]). Clearly, a similar variation is observed in $[Sn(L^2)Cl]^+$. It seems evident that the Sn–O bonds are longer than usual, in order to place the metal into the given conformation of the macrocycle. The macrocycle cannot accommodate Sn–O distances down to *ca.* 2.50 Å or less without a considerable increase in strain energy (see below). This preferred conformation would obscure any lengthening otherwise caused by lone pair repulsions and must enhance the 5*s* character of the lone pair. Hence, the usual structural signs of a stereochemically active lone pair, as apparent in *e.g.* $[PbL^3(H_2O)]^{2+}$, are greatly reduced. However, the unusual hexagonal bipyramidal[28] structure with the resulting vacant axial site offer evidence of some lone pair steric activity as indeed do the Mössbauer spectra.

*Other Structural Features.*—In common with other tin(II) structures there are weak interactions in (**1**) and (**2**) between the tin atoms and other atoms positioned around the direction of the tin lone pair. Thus, in (**1**) there is a long contact between tin and a chlorine atom of the $[SnCl_3]^-$ anion [Sn ··· Cl 3.656(6) Å, Cl–Sn ··· Cl, 165.6(1)°]; in (**2**) there is a long contact to a perchlorate oxygen [Sn(1) ··· O(13) 3.36(2) Å, Cl(3)–Sn ··· O(13) 152.7(4)°, Sn ··· O(13)–Cl(1) 103.8(8)° in (**2A**); Sn(2)–O(21) 3.38(2) Å, Cl(4)–Sn ··· O(21) 151.4(3)°, Sn ··· O(21)–Cl(2) 100.2(7)° in (**2B**)].

It should be noted that the essential geometry of the $[Sn(L^2)Cl]^+$ cation is unchanged from (**1**) to (**2**) as shown by the torsion angles and least-squares planes. This is consistent with weak axial interactions and relatively unimportant differences in packing forces.

*Mössbauer Parameters.*[2]—For $[Sn(L^2)Cl]^+$ in (**1**) and (**2**), the observed chemical shift was 3.889(3) mm $s^{-1}$ with respect to $BaSnO_3$; the quadrupole splitting was 2.109(7) mm $s^{-1}$ (78 K).

Taken in conjunction, Mössbauer spectroscopy and *X*-ray crystallography are a powerful combination. Information on electron distributions at probe nuclei given by the former is of particular value when viewed in the light of accurate structural details provided by the latter.

The Mössbauer quadrupole coupling constant contains information on relative distributions of tin 5*p*-electron densities over the bonds to tin and its lone pair. In covalent compounds the major contributions to quadrupole interactions at tin nuclei arise out of subtle imbalances in 5*p*-orbital occupations owing to deviations of electronic environments from cubic symmetry. For most tin(II) compounds the quadrupole interactions are considerably larger than those characteristic of tin(IV) compounds. This is generally attributed to the dominating effects of 5*p*-electron density localised in the lone pair and hence related to steric activity; although in reality the situation can be more complex (see below). The crystallographic data for $[Sn(L^2)Cl]^+$ establish its point group as being close to $C_{3v}$ (this takes into account the rippled $O_6$ group thereby negating $C_{6v}$, although the difference is not significant at the present level).

The electric field gradient axes, signs, and magnitudes of quadrupole interactions depend on the orderings and relative energies of the molecular orbitals associated with the probe atom.[14] In the case of tin, only the magnitude of the interaction is directly accessible and the large value for $[Sn(L^2)Cl]^+$ indicates only appreciable 5*p* electron imbalance. Since the 5*s* orbital has the same irreducible representation ($A_1$) as $5p_z$ they can mix, and, placing the lone pair along the crystallographically vacant axial position, the latter is explicitly described by contributions from a number of $a_1$ bonding and antibonding molecular orbitals. The magnitude of the quadrupole interaction shows that the difference in delocalising $5p_x$,$5p_y$ electron density into the *e* molecular orbitals and $5p_z$ into $a_1$, is appreciable. The principal electric field gradient axis is identified with the direction of the *lowest* degree of $5p$ electron delocalisation into molecular orbitals.[29] In this symmetry it is either directed along the chlorine–tin–lone pair axis or at 90°, *i.e.* within the $SnO_6$ plane. It would be presumptive to assume that the quadrupole splitting arises out of the lone pair possessing predominant $5p$ character.[14,30,31] However, the chemical shift gives additional information on lone pair character.

The chemical shift is a measure of the total *s*-electron density at the probe nucleus. Factors influencing chemical shifts[14,30] include the $5s$ character of the tin lone pair, delocalisation of $5s$-electron density into bonding levels, radial expansion of the $5s$ orbital owing to an increase in covalency in the bonding and the use of $5p$ orbitals which, because of their shielding properties, modify the total *s*-electron density at the probe nucleus. For tin(II) compounds in which the lone pair is sterically active, chemical shifts lie within the range 2.40—4.20 mm $s^{-1}$.[30] Hence, the comparatively high shift for $[Sn(L^2)Cl]^+$ is consistent with appreciable $5s$-electron density and is identified with the lone pair having high $5s$ character. This is also consistent with the analysis of crystallographic data on this and the other complexes (see above). Consequently, there are high degrees of $5p_x$,$5p_y$ character in the equatorial bonds to oxygen and $5p_z$ in the axial bond to chlorine. The large admixture of $5s$ character in the lone pair reflects the tendency of the system to move towards maximum occupation of the $5s$ orbital within limits imposed by the lattice and the conformation of the crown ether; the axial chlorine atom must take part in tying down the tin atom to the approximate $SnO_6$ plane, thereby aiding the process. Because of the reduced importance of the Pauli repulsions between the lone pair and the bonds the steric property of this lone pair is greatly reduced in the v.s.e.p.r. sense.

*Force Field Calculations.*—A recently developed method[32] using molecular mechanics for calculating macrocyclic hole sizes involves varying the M–L (L = donor atom) distance and calculating the strain energy. This is applied here to the $D_{3d}$ 18-crown-6 as found in (**1**) and (**2**). It is advantageous to use as symmetrical a model as possible, *i.e.* a hypothetical dichloro complex, $[Sn(L^2)Cl_2]$, rather than the actual $[Sn(L^2)Cl]^+$ because the resulting calculation is then less dependent upon the force constants for the L–M–L angle bending terms for which no accurate values are known. This approximation is also consistent with the observation that the stereochemical influence of the lone pair is evidently similar to that of the chlorine atom in (**1**) and (**2**). Starting co-ordinates for $[Sn(L^2)Cl_2]$ were taken from structure (**1**) but with an additional axial chlorine atom. Parameters for non-metal terms were taken from the MM2 program [33,34] which was used for all calculations. Values for metal terms were estimated (nomenclature from refs. 32 and 33) as follows: bond stretching Sn–Cl, $l_0$ 2.50 Å, $k_{(s)}$ 2.0 mdyn Å$^{-1}$, $c_{(s)}$ −2.0 Å$^{-1}$; angle deformation Cl–Sn–Cl, O–Sn–Cl, O–Sn–O, $\theta_0$ = 60, 90, 120, 180°; $k_b$ 0.30 mdyn Å rad$^{-2}$. The barriers M–O–C–C were fixed at values equivalent to those for C–O–C–C given in ref. 33; values for L–M–O–C were set at zero because of periodicity. Non-bonded interaction parameters for tin were $\varepsilon$ 0.27 kcal mol$^{-1}$ and $r^*$ 2.55 Å.

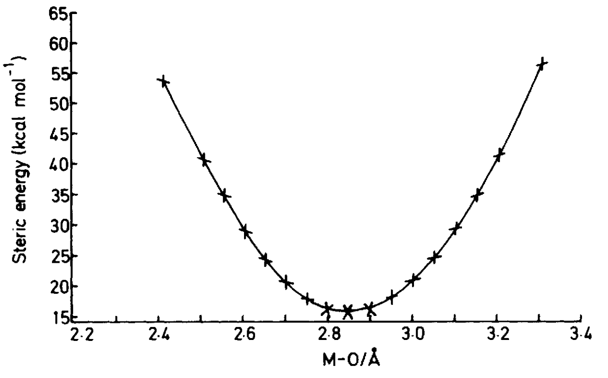

**Figure 5.** Plot of steric energy (kcal mol$^{-1}$) against M–O distances (Å) for the $D_{3d}$ conformation of 18-crown-6. Observed $[ML^2]^{n+}$ structures in the $D_{3d}$ conformation: M = $Hg^{2+}$ (mean M–O 2.85 Å), $Cd^{2+}$ (2.75 Å), $K^+$ (2.80 Å). $Cs^+$ and $Rb^+$ are too large and $Na^+$ and $Sn^{II}$ are too small for the hole and the resulting structures are considerably distorted (see text)

The Sn–O stretching force constants were then increased to 25.0 mdyn Å$^{-1}$, a value at least ten times greater than is realistic. Thus, the stretchings of these bonds become the dominant terms in the strain energy summation. This optimises the bond length at any input ideal length. Therefore after refinement, strain energy contributions are due entirely to the macrocycle conformation which has adjusted to fit this ideal bond length. Subsequently, the ideal Sn–O distance was varied and the calculation repeated. A plot of strain energy for various Sn–O bond lengths was obtained (Figure 5) which shows a minimum energy for a bond length of 2.85 Å. Inputting inordinately high values for the stretching force constant considerably reduces the significance of other metal parameters. The advantage of this is that it obviates the necessity of inputting accurate parameters which at the present state of application of molecular mechanics to inorganic systems are unattainable. It also means that Figure 5 is a measure of the 18-crown-6 hole size and is independent of the type of metal. The axial atoms are included to minimise distortions of the metal co-ordination sphere during the calculation. Various input values for the M–$L_{ax}$ bond stretching terms [$l_0$ and $k_{(s)}$] do not significantly affect the results. Provided the crown maintains an essentially $D_{3d}$ conformation we would expect the results to be independent of the nature of the axial ligands, and indeed be applicable to molecules such as $M(L^2)X$, without one, and $ML^2$ without both axial ligands.

Figure 5 confirms that in the observed $[ML^2]^{n+}$ $D_{3d}$ structures the metal fits into the cavity: M = Hg (mean M–O 2.85 Å),[35] Cd (2.75 Å),[35] $K^+$ (2.80 Å),[36] and confirms that the cesium cation is too large (3.15 Å)[21] for the cavity. This leads to the cesium cation being displaced 1.44 Å from the mean $O_6$ plane. The rubidium structure[37] shows a similar displacement (1.2 Å) for mean Rb–O 3.02 Å. By contrast, $Na^+$ and $Sn^{II}$ are too small, with the structural consequences described above.

An alternative is for the crown ether to adopt a different conformation with a smaller hole size and this has been observed for a few sodium complexes.[22–24] A previous molecular mechanics calculation[38] indicated that one of these distorted conformations had a lower energy with $Na^+$ than the $D_{3d}$ conformation. However, in this calculation partial charges on the crown ether oxygen atoms and on the atoms in the water molecule were included and were found to play an important role in stabilising this conformation. In the present work, we are concerned solely with the steric effect of fitting a metal into the macrocycle hole, and dipole interactions were therefore not included. We found no other conformation that gave a steric energy less than 45 kcal mol$^{-1}$ for any M–O distances.

Considering steric effects alone, the $D_{3d}$ conformation is most stable over a wide range of M–O distances. The other observed 18-crown-6 conformations are clearly stabilised by features such as dipole interactions, hydrogen bonds, other ligands, and possibly packing forces which overcome the steric advantages of the $D_{3d}$ conformation.

## Acknowledgements

We are grateful to the S.E.R.C. for support and Mr. A. W. Johans for assistance with the crystallographic investigations. We are also indebted to Dr. Reidar Lie, Head of Research, Borregaard Industries Ltd., Sarpsborg, Norway for donating the crown ether. The British Council (Dr. P. A. Thompson, Oslo) is thanked for the kind award of an academic travel grant (to M. G. B. D.).

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*Received* 24*th July* 1985; *Paper* 5/1270