Stereochemical Role of Lone Pairs in Main-group Elements. Part 4.[1] The Crystal Structure at 120 K of Bis(1,4,7,10,13-pentaoxacyclopentadecane)tin(II) Bis[trichlorostannate(II)], confirming the Sterically Inactive Tin Lone Pair†

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The crystal structure of $[SnL_2]^{2+}[SnCl_3^-]_2$ (L = 1,4,7,10,13-pentaoxacyclopentadecane) has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group $P2_1/a$, with $Z = 2$ in a unit cell of dimensions $a = 8.879(1)$, $b = 19.921(4)$, $c = 10.202(3)$ Å, and $\beta = 111.46(2)°$. The structure was refined to $R = 0.052$ for 3 859 observed reflections. There are two tin(II) sites (ratio 1 : 2); one is sandwiched between two crown molecules in a complex cation in which the tin lone pair is not stereochemically active; the other site is occupied by trichlorostannate(II) anions. The Mössbauer spectroscopic parameters of the complex cation are discussed in the light of the structure and are interpreted within a framework in which covalency is not considered insignificant.

Aside from relatively few exceptions, the dominant feature of *p*-block elements in their lower valence states is the role assumed by their lone pairs in producing irregular coordinations. Hitherto, all crystallographic studies on tin(II) complexes with neutral donor molecules have revealed tin(II) environments which are consistent with the tin lone pair being stereochemically active. The first indication that a *neutral* donor molecule might be capable of complexing tin(II) in ways which render its lone pair sterically inactive is the ^{119}Sn Mössbauer spectroscopic study by Herber and Carrasquillo[2] on a number of tin(II) complexes with the macrocyclic polyether 1,4,7,10,13-pentaoxacyclopentadecane (also known as 15-crown-5). We report here the crystal and molecular structure of the tin(II) chloride complex bis(1,4,7,10,13-pentaoxacyclopentadecane)-tin(II) bis[trichlorostannate(II)], $[SnL_2]^{2+}[SnCl_3^-]_2$.

Experimental

Preparation.—The complex was prepared by: (*a*) modifying Herber and Carrasquillo's method; 15-crown-5 (1.0 g) was added to tin(II) chloride dihydrate (2.06 g) in hot degassed methanol (5 cm^3); diffraction quality crystals were obtained after several hours; (*b*) warming tin(II) chloride dihydrate (2.06 g) in hydrochloric acid (2.5 mol dm^{-3}, 10 cm^3) with 15-crown-5 (1.10 g) in the presence of tin metal; suitable crystals were obtained after several days. The complex appears to be more susceptible to aerial oxidation, producing $SnCl_4(OH_2)_2L$,[3] than tin(II) chloride solutions that contain the smaller cyclic ether, 1,4-dioxan.[4]

Crystallography.—Crystal data. $C_{20}H_{40}Cl_6O_{10}Sn_3$, M = 1009.1, monoclinic, a = 8.879(1), b = 19.921(4), c = 10.202(3) Å, β = 111.46(2)°, U = 1 679.4 Å^3, Z = 2, $F(000)$ = 1 224, Mo-K_α radiation, λ = 0.710 69 Å, μ = 25.3 cm^{-1}. Absent reflections were consistent with the space group $P2_1/a$.

Intensity data collection and structure refinement. Crystals obtained from preparations (*a*) and (*b*) have identical cell dimensions and space group. A crystal from preparation (*a*) with the approximate dimensions 0.8 × 0.8 × 0.25 mm was mounted in a general orientation and intensity data collected at 120 K in the ω—2θ scan mode on a Nonius CAD4 automatic four-circle diffractometer out to θ = 30° using monochromatic Mo-K_α radiation. The crystal was stable during the data collection. The cell dimensions were determined from the refined setting angles of 25 reflections located by a search routine and the space group deduced from the systematic absences. The data were transferred to a VAX 11/750 computer, Lorentz and polarisation corrections applied, systematic absences rejected, and equivalent reflections merged. Of the 4 039 reflections measured 3 859 were deemed observed [$I_{net} > 3.0\sigma(I)$]. Scattering factors for tin(II) were used.[5] The CRYSTALS Issue 9 suite of programs[6] was used for the calculations and the structure solved by the heavy-atom method, corrected for absorption[7] (minimum and maximum corrections 0.919 and 1.153, respectively), and refined by full-matrix least squares on F in the space group $P2_1/a$ with anisotropic thermal parameters for all atoms. The crown molecules are disordered but since the type of disorder was easily found to take the form of a simple rotation about the SnL_2^{2+} molecular axis the disorder was readily unravelled by assigning weights of 0.5 to the carbon and oxygen atoms (the hydrogens were not placed); the anisotropic thermal parameters for each disorder-related ring non-hydrogen atom pair were refined together.

The final stage of the refinement was to assign each reflection a weight[8] $w = 1/\Sigma^n{}_r A_r T_r(X)$, where n is the number of coefficients, A_r, for a Chebyshev series, T_r is the polynomial function, and X is F_o/F_o(max.). The values of A_r which gave similar values of $w(F_o - F_c)^2$ over ranges of $(\sin\theta)/\lambda$ and F_o were 40.1, 51.8, and 17.9 giving final R = 0.052, and R' = 0.065. At convergence the root mean square (r.m.s.) shift/estimated standard deviation (e.s.d.) <0.3 and the highest peak in the difference Fourier map was 0.6 e Å^{-3}. The atomic positions are given in Table 1, and Table 2 contains the interatomic distances and valence angles.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates ($\times 10^5$ for Sn and $\times 10^4$ for the other atoms) with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Sn(1)	0	0	0
Sn(2)	−47 701(6)	−24 142(3)	53 221(5)
O(1)	−2 726(18)	−584(8)	285(15)
C(2)	−2 634(30)	−1 273(13)	734(27)
C(3)	−769(32)	−1 354(14)	1 981(29)
O(4)	359(17)	−1 161(7)	1 561(15)
C(5)	1 409(34)	−1 671(12)	1 454(28)
C(6)	2 587(32)	−1 455(13)	848(29)
O(7)	1 940(21)	−1 041(9)	−297(18)
C(8)	1 700(26)	−1 266(10)	−1 751(21)
C(9)	1 204(37)	−699(15)	−2 630(29)
O(10)	−95(16)	−332(7)	−2 542(14)
C(11)	−1 336(27)	−173(12)	−3 670(22)
C(12)	−2 974(23)	−191(10)	−3 540(20)
O(13)	−2 727(25)	−18(10)	−2 093(21)
C(14)	−4 175(34)	−35(14)	−1 794(33)
C(15)	−4 117(23)	−648(10)	−1 027(18)
O(1′)	1 516(18)	−650(7)	−1 595(14)
C(2′)	1 270(32)	−436(12)	−2 931(28)
C(3′)	−548(29)	−505(14)	−3 674(25)
O(4′)	−1 431(17)	−57(7)	−2 872(14)
C(5′)	−3 121(37)	−129(16)	−3 470(28)
C(6′)	−3 976(29)	79(12)	−2 638(27)
O(7′)	−3 209(19)	−117(9)	−1 188(17)
C(8′)	−3 958(26)	−724(11)	−743(20)
C(9′)	−3 221(33)	−786(12)	654(30)
O(10′)	−1 475(16)	−899(7)	1 134(14)
C(11′)	−1 096(24)	−1 563(11)	1 302(25)
C(12′)	675(21)	−1 684(8)	1 381(17)
O(13′)	1 198(24)	−1 232(8)	647(21)
C(14′)	2 351(34)	−1 518(14)	46(32)
C(15′)	1 807(22)	−1 354(9)	−1 386(17)
Cl(3)	3 453(2)	−1 456(1)	5 450(2)
Cl(4)	−3 819(3)	−1 773(1)	3 665(2)
Cl(5)	−2 560(2)	2 952(1)	2 563(2)

Results and Discussion

The crystal structure consists of the molecular ions [SnL_2^{2+}] and $2SnCl_3^-$. This confirms the formulation suggested by Herber and Carrasquillo in their interpretation of the Mössbauer spectrum.

The SnL_2^{2+} cation is shown in the Figure together with the atom numbering scheme. The C–C and C–O bond distances are comparable, within the standard deviations, with those reported for other cyclic polyethers.[1,3,4,9] To a good approximation, the conformation of the crown ethers in the SnL_2^{2+} ion is defined by the five oxygen atoms lying in a common plane. (We also note that synchrotron *X*-ray absorption studies [10] on methanol solutions of the same complex are also consistent with one of the several species present being the SnL_2^{2+} cation.)

Tin Co-ordination.—The tin atom in the SnL_2^{2+} cation is bonded to all five oxygens of each crown with bond lengths ranging from 2.63(2) to 2.79(1) Å. The immediate tin environment, $Sn(O_5)_2$, is best described as two pentagonal pyramids with their apices joining at the tin position and their bases staggered so that the tin atom lies on a crystallographic centre of symmetry (special position). The actual point group for SnL_2^{2+} is C_i and idealising the two O_5 groupings to planes gives point group D_{5d} for the $Sn(O_5)_2$ assemblage. Although apparent high-symmetry sites can arise out of the averaging of disordered molecules over the many unit cells which constitute the crystal, the actual symmetry of the SnL_2^{2+} cation is not obscured in this manner because the two $SnCl_3^-$ anions are related by the inversion centre at the cation. This conclusion is also fully consistent with the unusual Mössbauer parameters. The sandwich environment of the tin atom is reminiscent of that for tin(II) in decaphenylstannocene.[11]

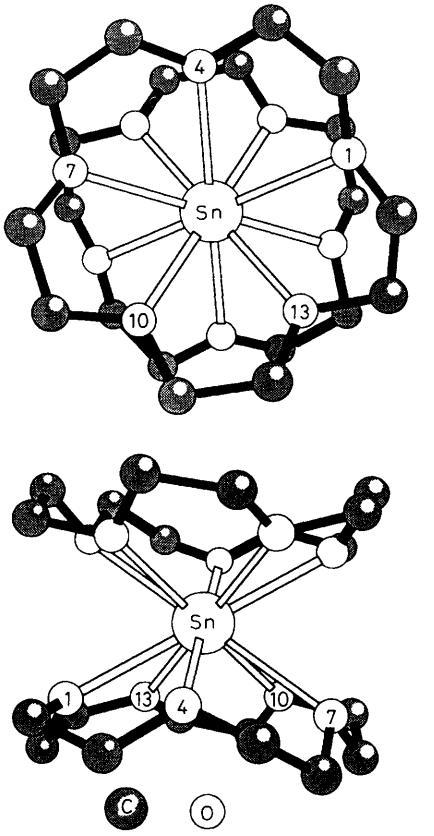

Figure. Structure of the SnL_2^{2+} cation viewed (top) along the direction normal to the mean O_5 plane and (bottom) along a direction 90° to the top view

Some Considerations on the Properties of the Lone Pair.—In order to analyse the stereochemical implications of the tin lone pair in the SnL_2^{2+} cation and to place its behaviour in perspective with other complexes we present the background to the description used here.

In general, lone-pair stereochemical 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. Frequently, a localised directed lone pair enables the stereochemistry to be rationalised by means of the valence-shell electron-pair repulsion (VSEPR) 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 (*e.g.* SnX_3 systems, as exemplified by the $SnCl_3^-$ anion in the present structure) and equatorial positions (*e.g.* SnX_4 systems) (X = any monodentate ligand), respectively.[4] In these cases the influence of the lone pair is self-evident, and its steric activity can be explicitly expressed as a number of symmetry orbitals.[4,9,12,13]

The physical foundation of the VSEPR model has been assumed to be an expression of the Pauli Exclusion Principle in forcing electron pairs to occupy different regions of space. However, this assumption has been questioned.[14] A more realistic view would appear to be more complicated. For example, Hall,[15,16] on the basis of extended-Hückel theory, suggests that Pauli repulsions in covalent molecules are

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Tin co-ordination			
Sn(2)–Cl(1)	2.509(2)	Sn(1)–O(4)	2.72(1)
Sn(2)–Cl(2)	2.499(2)	Sn(1)–O(7)	2.72(1)
Sn(2)–Cl(3)	2.491(2)	Sn(1)–O(10)	2.66(1)
Sn(1)–O(1)	2.79(1)	Sn(1)–O(13)	2.63(2)
Cl(1)–Sn(2)–Cl(2)	91.18(7)	O(4)–Sn(1)–O(7)	119.8(4)
Cl(1)–Sn(2)–Cl(3)	94.10(7)	O(4)–Sn(1)–O(10)	108.2(4)
Cl(2)–Sn(2)–Cl(3)	93.23(7)	O(4)–Sn(1)–O(13)	105.9(5)
O(1)–Sn(1)–O(4)	120.2(4)	O(7)–Sn(1)–O(10)	118.7(5)
O(1)–Sn(1)–O(7)	108.8(4)	O(7)–Sn(1)–O(13)	108.1(5)
O(1)–Sn(1)–O(10)	108.0(4)	O(10)–Sn(1)–O(13)	120.2(4)
O(1)–Sn(1)–O(13)	121.0(4)		
(*b*) 15-Crown-5 molecule			
O(1)–C(2)	1.43(3)	C(9)–O(10)	1.41(3)
C(2)–C(3)	1.57(4)	O(10)–C(11)	1.30(2)
C(3)–O(4)	1.41(3)	C(11)–C(12)	1.60(3)
O(4)–C(5)	1.49(2)	C(12)–O(13)	1.41(3)
C(5)–C(6)	1.54(3)	O(13)–C(14)	1.42(3)
C(6)–O(7)	1.32(3)	C(14)–C(15)	1.38(3)
O(7)–C(8)	1.51(2)	C(15)–O(1)	1.46(2)
C(8)–C(9)	1.42(3)		
C(15)–O(1)–C(2)	111.6(9)	C(8)–C(9)–O(10)	109.4(19)
C(3)–C(2)–O(1)	113.8(13)	C(9)–O(10)–C(10)	115.4(9)
C(2)–C(3)–O(4)	115.6(17)	C(11)–O(13)–C(14)	113.6(9)
C(3)–O(4)–C(3)	113.6(9)	O(13)–C(14)–C(15)	108.7(18)
C(6)–O(7)–C(8)	113.8(9)	O(1)–C(15)–C(14)	108.8(17)
C(9)–C(8)–O(7)	107.3(14)		

important only for those *between* bonds and that stereochemical activity results not *primarily* from Pauli forces, but from a system's desire to reduce the total energy through maximum population of the lower valence *s* orbital. This end is achieved by appropriate changes in geometry which also attend the other, interdependent, contributions to the overall energy of the system. 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 give rise to stereochemical activity in the VSEPR sense. A lone pair with pure *s* character has essentially antibonding properties[9] since for the relevant point group there is always a combination of ligand orbitals with the same symmetry properties as the *s* orbital that permits interaction. Such a lone pair is designated non-stereochemically active, in the VSEPR sense. Yet, in a broader sense, an *s*-character lone pair can be regarded as being sterically active because it is the cause of long bonds, and also because it is the result of the system being able to adjust its geometry so that the energy is reduced by optimum population of the *s* orbital. Donaldson and Grimes[17] and Ng and Zuckerman[18] reviewed the status of lone-pair chemistry up to the mid-1980s for Group 4 elements and more generally, respectively.

Specifically in the case of the present compound, the influence of the crown ether on the tin lone pair is central when discussing the stereochemistry of the cation. Since the tin(II) atom lies on a centre of symmetry (point group C_i) the lone pair is necessarily precluded from being stereochemically active. It is this characteristic which makes the complex especially interesting in the context of tin chemistry because only a few other tin(II) materials (such as $CsSnCl_3$ above 363 K, $CsSnBr_3$, and $CsSnI_3$ all of which have the ideal perovskite structure,[19] and SnSe and SnTe with the cubic NaCl structure[20]) contain stereochemically inactive tin lone pairs. It has been suggested that the unusual properties (such as semiconductivity and intense colours) and the high symmetry of the tin(II) sites in these extended structures are a consequence of the $5s^2$ electrons delocalising into low-lying bands of the crystals.[19] The high-symmetry tin site in the present structure is even more unusual because the crystal lattice is not macromolecular but instead is built out of discrete molecular cations and anions. It would seem apparent that the energetics underlying the structure are rooted in the special ability of the crown to interact all five of its oxygen atoms with the tin(II) cation.

We note that the present ligand behaves in an identical fashion towards the acceptor molecule antimony(III) chloride,[1] and although the resulting complex $SbCl_3 \cdot L$ is a molecular adduct, the bonds to antimony are evidently similar to those in tin. The explanation which springs most readily to mind for the antimony acceptor forming a molecular adduct instead of the crown-complexed Sb^{3+} cation that would have been reminiscent of the tin complex is that the energy associated with the crown complexing a divalent tin cation more than compensates the energy needed to ionise tin to the ideal Sn^{2+} cation. This is less than half that (being 2 119.8 and 4 872.0 kJ mol^{-1}, respectively) for the isoelectronic ideal Sb^{3+} cation.[21]

This difference notwithstanding, the structural data show that Sn^{2+} and antimony(III) chloride clearly exert similar influences on the ligands. Despite tin(II) and antimony(III) being of comparable size, the bond distances to the oxygens are significantly longer [2.787(5)—2.997(4) Å] in the antimony complex than they are in the complexed Sn^{2+} cation [2.63(2)—2.79(1) Å]. This is clearly consistent with somewhat enhanced acceptor properties for Sn^{2+} relative to antimony(III) chloride. It is also clear when comparing shorter Sn–O bond lengths, such as 2.527(5) Å in dichloro(1,4-dioxane)tin(II),[4] that the individual interactions are relatively weak. It is shown below that a contributing factor to the long bonds must be the antibonding influence of the sterically inactive tin lone pair because appreciable localisation of electron density in the 5*s* orbital hinders closer approaches.[4] The cation is SnL_2^{2+}, rather than Sn^{2+}, and therefore designating the tin atom a 'bare' *spherical* Sn^{2+} is fallacious. The difference is not semantic; the model advanced here has consequences for interpreting the Mössbauer chemical shift and is particularly important for placing the hypothetical Sn^{2+} ($5s^2$) ion on the general Mössbauer chemical shift scale.

Mössbauer Parameters.[2]—Taken together, Mössbauer spectroscopy and *X*-ray crystallography are a powerful combination, with the former providing information on electron distributions at a probe nucleus which is particularly valuable when viewed in the light of accurate geometrical details provided by the latter.

The Mössbauer parameters of interest are the chemical shift and the quadrupole coupling constant. The quadrupole coupling constant contains information on the relative distributions of tin 5*p* electron densities over all the tin bonds and its lone pair. In covalent compounds the major contributions to quadrupole interactions at the tin nuclei arise out of the subtle imbalances in 5*p* orbital occupations (*i.e.* the 5*p* orbitals are non-degenerate) that result from deviations from cubic symmetry of the electronic environments. For most tin(II) compounds the quadrupole interactions are larger than those characterising tin(IV) compounds. This is generally attributed to the dominating effects of 5*p*-electron density localised in the lone pair and is hence related to steric activity, although in reality, as pointed out below, the situation can be more complex.

For cubic electronic symmetries (and of course spherical symmetry for a hypothetical isolated atom or ion) there is no electric field gradient because the 5*p* orbitals are then degenerate. Since the crystallographic symmetry at the probe nucleus is necessarily the same (at least formally) as the electronic, cubic environments have degenerate *p* orbitals and therefore the tin absorption is characterised by a singlet in the

Mössbauer spectrum. The C_i point group of SnL_2^{2+} means that since the tin atom lies on a centre of symmetry the lone pair relates to the 5*s* orbital with no 5*p* admixture (see above) and accordingly does not contribute to the quadrupole interaction; this point group implies that the $5p_x$, $5p_y$, and $5p_z$ degeneracies belonging to spherical or cubic environments are lifted. We note that whilst admixtures of 5*d*-orbital character are not excluded on symmetry reasons alone (since the *d* orbitals in C_i symmetry have the same symmetry as the 5*s*), for tin(II) compounds significant participation of 5*d* orbitals has been considered unlikely in view of the energy separation between the 5*p* and 5*d* orbitals.[22]

The orientation of electric-field gradient axes, and the signs and magnitudes of quadrupole interactions, depend on the orderings and relative energies of the molecular orbitals associated with the probe atom. In the case of tin, only the magnitude of the splitting is directly accessible and the zero (or unresolved and hence very small) quadrupole splitting for SnL_2^{2+} shows that there is no (or at least negligible) electron imbalance in the 5*p*-orbital populations, *i.e.* they are all close in energy if not degenerate.

However, it is a caveat that whereas a cubic environment cannot possess an electic-field gradient the reverse is not necessarily true. Cases are known[23,24] in which non-cubic crystallographic sites produce what might be termed *pseudo* cubic electronic environments where obviously the 5*p*-orbital degeneracy is hardly lifted within spectral resolution, *i.e.* there is no significant imbalance in 5*p* occupations. This is clearly the case for the SnL_2^{2+} ion because the tin atom is unequivocally in a non-cubic environment.

The chemical shift is a measure of the total *s*-electron density at the probe nucleus. Factors influencing chemical shifts[13,23] include the percentage *s* character of the tin lone pair, delocalisation of 5*s*-electron density into bonding levels, radial expansion of the 5*s* orbital owing to an increase in covalency in the bonding, and the use of 5*p* 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} relative to $BaSnO_3$.[23]

What makes the present compound unusual compared with most other tin(II) compounds with zero splittings[23,24] is the relatively high value of the chemical shift (4.59 ± 0.05 mm s^{-1} relative to $BaSnO_3$). The simplest interpretation is that originally forwarded[2] in which the high shift is attributed to the ionic $5s^2$ configuration, *i.e.* a 'bare' Sn^{2+} cation. However, from the crystallographic data it is apparent that the true picture is more involved; what the chemical shift does show is that considerable electron density is localised in the 5*s* orbital and we interpret the data as reflecting significant covalent interactions (see below) between Sn^{2+} and the two crown rings. This necessarily leads to transfer of electron density from the relevant ligand symmetry orbitals into the 5*p* orbitals on tin. Since 5*p*-electron density shields the nucleus to some extent from the 5*s* electrons, a pure Sn^{2+} cation interacting with the crown molecules *via* ion-dipole forces and not through covalent bonding would exhibit considerably higher chemical shifts than that observed here. We turn now to other evidence which is consistent with this view.

To date, at least four other tin compounds have also been correlated with 'bare' Sn^{2+} ions. The Mössbauer chemical shifts for these compounds are somewhat higher[25—28] than the shift for SnL_2^{2+}. Except for one of them,[27] no quadrupole splittings could be resolved. If the same arguments are used for interpreting the chemical shifts and absence of quadrupole interactions for these as originally put forward for the 15-crown-5 complex, then one would have to conclude that the tin lone pair is not sterically active for all these cases. Yet, the *X*-ray structure of one of these, $Sn(SbF_6)_2(AsF_3)_2$ with a chemical shift of 4.66 ± 0.04 mm s^{-1}, emphasises the danger of over interpreting Mössbauer parameters in the absence of crystal-structure information because the tin(II) site here is actually far from being cubic or high symmetry and is instead distorted in a manner fully consistent with a *sterically active* tin lone pair. Furthermore, the exception with the non-zero quadrupole splitting,[28] 3-Sn-1,2-$B_9C_2H_{11}$, displays a high shift (4.67 ± 0.04 mm s^{-1}) and a very large quadrupole splitting (3.83 ± 0.04 mm s^{-1}). A splitting of this magnitude shows very large imbalances in 5*p* occupations (but does not give information on the total 5*p* electron density) which result from the considerable lifting of 5*p* degeneracy (which of course is synonymous with distortion from cubic symmetry) as 5*p* electron densities are delocalised into molecular orbitals. The shift seems to indicate that the overall delocalisation is extensive; but in the absence of crystallographic data on this material any further discussion of the result would be speculative.

The Bonding in SnL_2^{2+}.—In order to facilitate visualising the contributions from the crown oxygen lone pairs to the Sn–O interactions we initially force each of the two sets of five crown oxygens to lie on a common plane. The symmetry of an isolated SnL_2^{2+} is then idealised to D_{5d} (but later we accept that the geometry adjusts to the observed C_i symmetry under various influences including conformational and lattice energies). Ten symmetry orbitals are constructed out of the two identical sets (designated A and B) of the $(O)_5$ lone pairs that are directed towards the tin atom by the combinations A + B and A − B, and since the rings are related by inversion the two combinations are *ungerade* and *gerade* respectively. Constructing the complete set of symmetry orbitals for the oxygen lone pairs for the rings together yields three sets of symmetry orbitals which are filled by the ten pairs; a pair (A_{1g} and A_{2u}) with no node, a higher set (E_{1g} and E_{1u}) with a single node, and a set at even higher energy (E_{2g} and E_{2u}) with two nodes.

With an idealised D_{5d} point symmetry the tin atomic orbitals transform irreducibly as A_{1g} (5*s*), E_{1u} ($5p_x$, $5p_y$), and A_{2u} ($5p_z$) symmetries and the Sn–O bonds are associated with the bonding molecular levels $(a_{1g})^2(a_{2u})^2(e_{1u})^4$, the non-bonding levels $(e_{1g})^4(e_{2g})^4(e_{2u})^4$, and the filled antibonding level $(a_{1g})^{*2}$. The latter level is largely identified with the 5*s* orbital on tin, the lone pair. The quadrupole interaction is related to the energy difference (imbalance) between the E_{1u} and A_{2u} levels in this idealised point group.

The actual point group means that all of the two-degenerate orbitals are split (paralleling the geometrical distortions) so that the 5*s* and 5*p* orbitals now transform with A_g or A_u symmetries, respectively. Any steric activity of the lone pair would depend on the degree of admixtures of the 5*p* wavefunctions with the 5*s* wavefunction, but since the two types of orbital have different symmetries they do not mix and the lone pair has 5*s* character. The ligand-group orbitals and the appropriate tin orbitals form a bonding a_g and an antibonding a_g^* symmetry level [which identify with the $(a_{1g})^2$ and $(a_{1g})^{*2}$ orbitals of D_{5d}] plus nine with A_u symmetry, but the tin lone pair retains its 5*s* character. The a_u orbitals are associated with the 5*p* orbitals and have mixed p_x,p_y,p_z contributions (they have the same symmetry) and the quadrupole interaction or *p*-electron imbalance is therefore negligible.

In conclusion, the formal Sn^{2+} cation in SnL_2^{2+} is covalently bonded to the 15-crown-5 ligands [in essentially the same manner as the $SbCl_3$·L adduct]. As is also the case for the antimony adduct the tin 5*p* electron density is extensively delocalised over the molecular orbitals whereas the tin 5*s* electron density is identified with the filled antibonding level; the long Sn–O bonds and the Mössbauer chemical shift are consistent with the antibonding electron density being localised to a large extent in the 5*s* orbital. Although these bonds are individually weak, but somewhat stronger than in the antimony adduct, the sum of their interactions is quite strong. The observed geometry represents a drive to reduce the total energy of the system through maximum population of the 5*s* orbital. All in all, a bare (hypothetical) Sn^{2+} ion that interacts with ligands in an essentially purely electrostatic manner must have a very much higher shift.

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