Stereochemical Role of Lone Pairs in Main-group Elements. Part I. Structure and Bonding in Dichloro(1,4-dioxan)tin(II)

By **Edward Hough** and **David G. Nicholson,*** Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space-group *C*2/*c* with $Z = 4$ in a unit cell of dimensions $a = 7.825(1)$, $b = 11.688(2)$, $c = 9.172(1)$ Å, $\beta = 98.01(1)°$. The structure was refined by least-squares methods to *R* 0.043 for 1 209 observed reflections. The structure consists of $SnCl_2$ units linked by dioxan ligands, in the chair conformation, to form polymeric arrays. The stereochemical activity of the tin lone pair is clearly evident and the metal–ligand bonding is discussed in terms of the tin 5*s* and 5*p* valence orbitals, without recourse to significant 5*d* contributions.

THE stereochemical influence of lone pairs in *p*-block elements in lower valence-states has attracted considerable attention.[1,2] In many instances it has been established that the lone pair plays a stereochemical role, although a number of examples are now known where it is stereochemically inactive.[3] In the case of tin(II) chemistry much of the experimental information is consistent with the lone pair being stereochemically active.[4] However, although this is a dominant feature exceptions have recently been reported: the high-temperature modifications of caesium trihalogenostannate(II) [5,6] and one of the tin sites in tin(II) iodide.[7]

In addition to this aspect of tin(II) chemistry certain other features require structural elucidation. A number of tin(II) compounds act as acceptors towards suitable donor molecules. Many behave as monofunctional acceptors, but some complexes are known which contain additional ligands.[4] I.r. and ^{119}Sn Mössbauer spectroscopic studies of multiligand tin(II) adducts have established that the additional donor molecules may be either bonded to tin or present only for crystal packing purposes.[8,9] Previously, two single-crystal structure determinations had been performed on two tin(II) adducts in which the donors are neutral ligands. The structure of one of these, tin(II) chloride dihydrate, has been shown by two studies [10,11] actually to correspond to aquadichlorotin(II) hydrate, $SnCl_2(OH_2)\cdot H_2O$. The results of both investigations are consistent with only one water molecule being bonded to tin with the second held in the lattice by hydrogen bonds. The second complex is sulphatobis(thiourea)tin(II),[12] $Sn(tu)_2SO_4$, (tu = thiourea), which differs from $SnCl_2\cdot 2H_2O$ in that both ligands, although not equivalent, are bonded to tin. In both these structures the influence of the lone pair is evident.

The ligand molecules in the 1 : 1 complexes of tin(II) halides with 1,4-dioxan, 1,4-thioxan, and 1,4-dithian could conceivably exist in either the boat or the chair conformation. Thus, they could act as either uni- or

---

[1] R. J. Gillespie, *J. Chem. Educ.*, 1970, **47**, 18.

[2] L. S. Bartell, *J. Chem. Educ.*, 1968, **45**, 754.

[3] D. S. Urch, *J. Chem. Soc.*, 1964, 5775.

[4] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

[5] J. Barret, S. R. A. Bird, J. D. Donaldson, and J. Silver, *J. Chem. Soc.* (*A*), 1971, 3105.

[6] D. E. Scaife, P. F. Weller, and W. G. Fisher, *J. Solid-State Chem.*, 1974, **9**, 308.

[7] R. A. Howie, W. Moser, and I. C. Trevena, *Acta Cryst.*, 1972, **B28**, 2965.

[8] J. E. Cassidy, W. Moser, J. D. Donaldson, A. Jelen, and D. G. Nicholson, *J. Chem. Soc.* (*A*), 1970, 173.

[9] J. D. Donaldson, D. G. Nicholson, and B. J. Senior, *J. Chem. Soc.* (*A*), 1968, 2928.

[10] B. Kamenar and D. Grdenić, *J. Chem. Soc.*, 1961, 3954.

[11] H. Kiriyama, K. Kitahama, O. Nakamura, and R. Kiriyama, *Bull. Chem. Soc. Japan*, 1973, **48**, 1389.

[12] J. D. Donaldson, D. G. Nicholson, D. C. Puxley, and R. A. Howie, *J.C.S. Dalton*, 1973, 1810.

bi-dentate donors. From i.r. spectra it has been suggested [13] that the ligand molecules in these adducts adopt the chair conformation and that accordingly they are non-chelating, since this would require the boat form. As there is no spectral evidence for two distinct C–O–C or C–S–C ring stretching vibrations for the 1,4-dioxan and 1,4-dithian adducts, it seems likely that the structures are polymeric. In order to clarify this situation we have determined the crystal structure of dichloro(1,4-dioxan)tin(II),$SnCl_2(1,4-C_4H_8O_2)$.

EXPERIMENTAL

Preparation.—The complex was prepared (*a*) by adding 1,4-dioxan (0.03 mol) to tin(II) chloride (0.01 mol) in hot ethanol (5 cm^3) and cooling to room temperature,[13] or (*b*) by cooling a hot solution of tin(II) chloride in 1,4-dioxan.

Crystal Data.—$C_4H_8Cl_2O_2Sn$, $M = 277.9$, Monoclinic, $a = 7.825(1)$, $b = 11.688(2)$, $c = 9.172(1)$ Å, $\beta = 98.01(1)°$, $U = 830.6$ Å^3, $D_m = 2.1$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.22$ g cm^{-3}, $F(000) = 528$. Mo-K_α radiation, μ(Mo-K_α) = 36.7 cm^{-1}. Absent spectra, consistent with space-groups $C2/c$ and Cc. The density of the complex implies a unit-cell occupancy of four and one molecule in the asymmetric unit if the space-group is Cc whereas, in the alternative, $C2/c$, the molecule is required to be centrosymmetric or two-fold symmetric.

Intensity Data Collection and Structure Refinement.—Since the complex loses dioxan within a relatively short time, crystals were sealed in glass capillaries. Crystals obtained from preparations (*a*) and (*b*), although consistent in cell dimensions, showed significant differences in behaviour during data collection. Those prepared by method (*a*) exhibited extremely rapid and large random intensity fluctuations which appeared to arise from movements of the intensity maxima by as much as 0.04° in ω. Since the effect was most prominent for reflections in the $h0l$ zone it may imply laminar twinning or dislocation. After examination of some twenty specimens from preparation (*a*) it was found that only crystals obtained from preparation (*b*) were free from this effect and one was selected for the collection of intensity data on an automatic Syntex $P\bar{1}$ four-circle diffractometer out to θ 30° by use of monochromatised Mo-K_α radiation. The crystal, dimensions 0.37 × 0.23 × 0.12 mm, was stable during data collection. It was mounted in a general orientation in order to minimise multiple reflections. Of the 1 243 reflections measured 1 209 were classified as observed, *i.e.* $I_{net} > 2.58\sigma(I)$. Data were corrected for Lorentz, polarisation, and absorption effects. Scattering factors for light atoms were from ref. 14*a* and for tin from ref. 14*b*; solution and refinement were carried out by use of the '*X*-Ray '70' system of programmes.[15]

The solution of a Patterson synthesis in the space-group $C2/c$ places the tin atom either at the origin, thereby requiring it to be in a centrosymmetric environment, or on the two-fold axis at $0,y,1/4$. The former is highly unlikely on chemical grounds and can therefore only be accommodated if pseudosymmetry is introduced at the tin site by disorder in the crystal lattice. In space-group Cc the tin atom is in the general position $x,0,z$ with no special symmetry requirements. Attempted refinement of a disordered form of the structure in $C2/c$ was unsuccessful. However, refinement was possible in both the other cases and R converged to 0.042 (Cc) and 0.043 ($C2/c$),with anisotropic temperature factors for all atoms.

We prefer the solution based on $C2/c$ for the following reasons. (*a*) Although the R factors are very similar, only half of the parameters required in Cc are involved in $C2/c$. (*b*) The standard deviations in Cc are some four times larger. (*c*) The bond lengths and angles for the dioxan unit are in considerably better agreement with those reported for other dioxan complexes (see below). It should be noted that the Cc solution places the tin atom in a very similar environment, since it is only slightly distorted from two-fold symmetry, and for the present level of discussion this difference is not significant.

TABLE 1

(*a*) Final positional parameters (× 10^5 for Sn, × 10^4 for other atoms) with estimated standard deviations in parentheses

Atom	x	y	z
Sn	0 0000	0 907(6)	25 000
Cl	0 240(3)	1 580(2)	4 433(2)
O	3 233(6)	03 07(4)	2 659(6)
C(1)	4 073(10)	1 302(7)	2 198(15)
C(2)	4 058(10)	−0 691(7)	2 180(12)

(*b*) Anisotropic temperature factors,* with standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	29.3(3)	35.4(3)	28.2(3)	0.0	6.5(2)	0.0
Cl	60(1)	44(1)	33.4(7)	−4.2(8)	5.7(7)	−7.2(6)
O	23(2)	40(2)	61(3)	0.9(2)	10(2)	1(2)
C(1)	29(4)	38(4)	151(10)	1(3)	13(5)	24(5)
C(2)	27(3)	38(4)	105(7)	2(3)	4(4)	−11(4)

* The values listed are 10^3U_{ij}, where the temperature factor has the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + U_{12}a^*b^*hk + U_{23}b^*c^*kl + U_{13}a^*c^*hl)]$.

TABLE 2

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Tin co-ordination			
Sn–Cl	2.474(2)	Sn–O	2.527(5)
Cl–Sn–Cl′	90.52(7)	O–Sn–O′	168.5(2)
O–Sn–Cl′	86.9(1)	Cl′–Sn–O′	85.0(1)
(*b*) Dioxan groups			
C(1)–O	1.43(1)	C(1)–C(1′)	1.48(1)
C(2)–O	1.43(1)	C(2)–C(2′)	1.51(1)
C(1)–O–C(2)	109.1(7)	C(1)–C(1′)–O	110.9(8)
C(2)–C(2′)–O	109.8(7)	C(1)–O–Sn	124.3(4)
C(2)–O–Sn	113.0(4)		

The atomic positions and thermal parameters are given in Table 1, and Table 2 contains the interatomic distances and valence angles. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 21759 (3 pp., 1 microfiche).*

DISCUSSION

The crystal structure (Figure 1) consists of $SnCl_2$ units separated by a unit-cell translation in the a direction and

---

* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies).

[13] J. D. Donaldson and D. G. Nicholson, *J. Chem. Soc.* (*A*), 1970, 145.

[14] (*a*) 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962; (*b*) D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[15] '*X*-Ray' program system, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report 67 58, 1967, revised version of 1970.

linked by dioxan molecules to form linear polymeric arrays. The tin atoms in these arrays are connected to two *c*-glide related tin atoms by long-range Sn · · · Cl interactions, thereby forming sheets of $SnCl_2$ units. A second, interposing, set of polymeric arrays is generated by the face-centring translation. The dioxan molecules are in the chair conformation and their bond parameters are similar to those found in other dioxan complexes.[16,17]

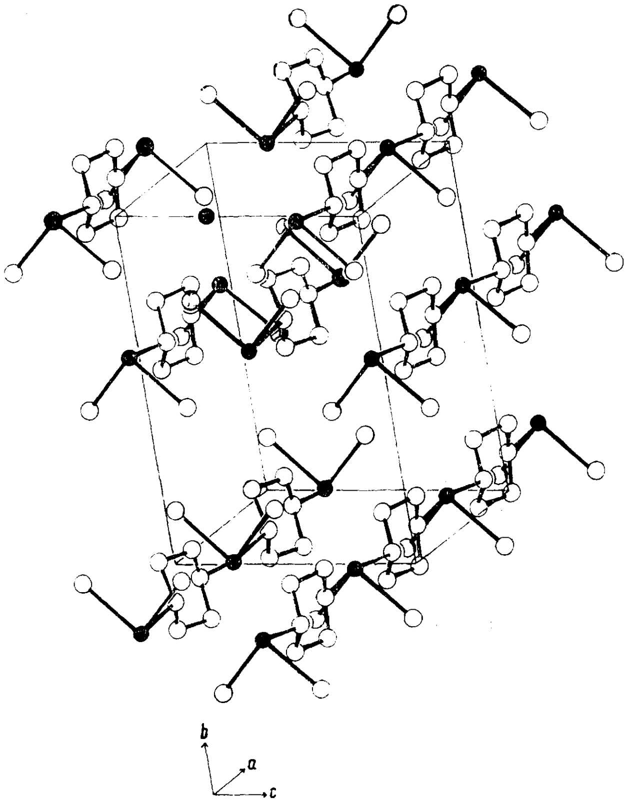

FIGURE 1 Crystal structure of dichloro(1,4-dioxan)tin(II)

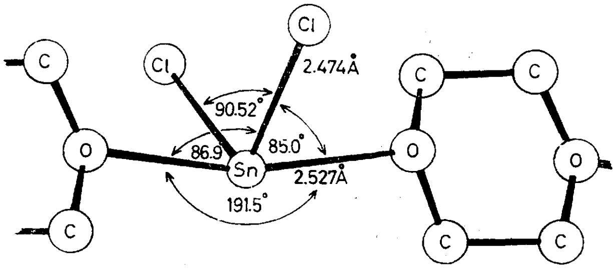

FIGURE 2 Part of the polymeric array showing the Sn environment (two-fold axes through the tin atom and the dioxan molecule omitted)

Tin Co-ordination.—The tin environment (Figure 2) is two-fold symmetric by symmetry requirements, but is close to point-group C_{2v}. The co-ordination polyhedron is best described as distorted five-co-ordinate with the fifth position evidently being occupied by a stereochemically active lone pair. This arrangement is fully consistent with the distorted trigonal bipyramid predicted by the VSEPR model[1] for discrete AX_2Y_2E species (A = central atom; E = lone pair; X, Y = ligands). Whilst the two Cl–Sn bonds form a right-angle the O–Sn–O bonding angle is only 11° short of linearity. Repulsion forces between the Sn–O bonding electrons and the tin lone pair may be relieved either by a reduction in the O–Sn–O angle or by lengthening of the Sn–O bonds. The dominating effect of the tin lone-pair and its tendency to repel the oxygen atom is opposed by the role of dioxan as a link between $SnCl_2$ units since a reduction in the O–Sn–O angle must result in distortion of the oxygen environments. The Sn–O bonds (2.527 Å) are some 0.2 Å longer than that in tin(II) chloride dihydrate,[11] and even longer (by 0.24 and 0.39 Å) than those in the β-diketonate, bis(1-phenylbutane-1,3-dionato)-tin(II).[18] This compound is more appropriate for comparison because it exhibits the same co-ordination number and point-group for tin as the present structure. However, whereas the diketonate structure consists of discrete molecules the dioxan adduct is polymeric. Moreover, although there is some constraint imposed on the bond angles subtended at tin in the diketonate by the oxygen atoms being part of two chelating units, the considerably larger deviation (30°) of the axial O–Sn–O bonds from linearity and the much shorter Sn–O bonds do suggest an increase in stereochemical activity of the lone-pair. It therefore seems evident that the lone-pair–bond-pair repulsions in the dioxan adduct are reduced by bond-lengthening. This clearly results in weaker Sn–O bonds which is also consistent with the ready loss of dioxan from the adduct at room temperature. An interesting feature is that, in contrast to the situation in $SnSO_4 \cdot 2tu$,[12] where there are major differences between the two Sn–S bond lengths (2.62 and 2.86 Å), both oxygen atoms in the present compound are similarly bound to tin.

The Sn–Cl interatomic distances are shorter than those in the dihydrate (2.50 and 2.56 Å),[11] but similar to those in the trichlorostannate(II) anion (2.440, 2.445, and 2.447 Å).[19] The two long-range Sn · · · Cl (3.451 Å) interactions which connect the polymeric $SnCl_2$–dioxan arrays complete a distorted octahedral co-ordination about tin. Interactions of this type are described as secondary bonds by Alcock,[20] and defined as those interatomic distances, often regarded as nonbonding, which are longer than normal bonds but shorter than van der Waals distances.

There has been much discussion concerning the nature of bonding in compounds of main-group elements. This applies especially to the question of whether or not

---

[16] M. Davies and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.

[17] O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 1953.

[18] P. F. R. Ewings, P. G. Harrison, and T. J. King, *J.C.S. Dalton*, 1975, 1455.

[19] J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *Inorg. Chem.*, 1973, **12**, 1668.

[20] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 2.

d orbitals are significant to σ-bond formation.[21-24] In the case of tin(II) chemistry 1 : 1 complexes between tin(II) acceptors and various unidentate donors are well known. This is consistent with the available $5p$ orbital in tin(II) acceptor compounds.[4] Simple descriptions in terms of hybridisation language place considerable weight on the importance of d-orbital participation when the co-ordination number exceeds four (including stereochemically active lone pairs) and sp^3 hybridisation becomes inadequate. This model requires the use of d orbitals in order to accommodate the excess of electrons. Thus, in order to form a complex with a second donor molecule, tin would have to make use of its $5d$ orbitals. In view of the energy separation between the tin $5p$ and $5d$ orbitals this is unlikely.[4]

Alternatively, the tin environment may be described in terms of a qualitative MO picture without recourse to significant $5d$ involvement, although a small contribution from higher orbitals will be contained within the total wavefunction. The $5s$ and $5p$ valence orbitals in the fragment $SnCl_2O_2$ (idealised to point-group C_{2v}) transform irreducibly as $A_1(s)$, $B_1(p_x)$, $B_2(p_y)$, and $A_1(p_z)$. Following a similar treatment used in describing the electronic structures of antimony(III) halides,[25] the electronic structure would contain four lowest-energy ($1a_1$, $1b_1$, $1b_2$, $2a_1$) bonding levels which possess major ligand character, and a higher-energy level which is largely associated with the tin lone pair. It seems reasonable to infer that the latter can be identified as the $3a_1$ level, as the crystallographic environment of the tin atom is consistent with the lone pair being directed along the symmetry axis. Since the tin $5s$ and $5p_z$ orbitals have the same symmetry they can mix, so that the $3a_1$ level represents a large degree of the overall $5s$ contribution to the lone pair. Ligand lone-pair a_1 group orbitals can also interact with the tin lone pair thereby resulting in stabilised (bonding) and destabilised (antibonding) higher levels. As was previously pointed out,[25] the lone pair on the central atom is explicitly described in terms of contributions from a number of a_1 symmetry molecular orbitals and nonplanarity is mainly attributable to the balance attained between bonding and antibonding a_1 orbitals. The weak Sn–O bonds can be explained if they are mainly associated with the a_1 levels and the normal Sn–Cl bonds together with the Cl–Sn–Cl angle would then be predominantly associated with the $1b_1$ and $1b_2$ levels. The two more distant chlorine atoms are largely associated with higher levels. These relate to lone pairs essentially localised on these ligands.

In any discussion on stereochemistry at a particular site in a solid-state compound, constraints imposed by the crystal lattice must be considered. In the present structure the polymeric nature of the complex must constrain the O–Sn–O angle (see above). This means that the energy of the antibonding contributions to bonding cannot be further reduced and as a result the Sn–O bonds are rather long and weak.

It is of special interest to compare this situation with that prevailing in bis(1-phenylbutane-1,3-dionato)tin(II) where the tin(II) atom in the fragment SnO_4 again lies on a diad axis and has approximate C_{2v} symmetry. The constraint on the O–Sn–O angle present in the dioxan adduct is not present here and the axial O–Sn–O bond angle attains 150.4°. This considerable reduction in angle is matched by much shorter axial Sn–O bond lengths (2.290 Å). We feel that these differences are consistent with the lower energies of the $3a_1$ and higher a_1 levels, which permit reduced antibonding contributions to the axial Sn–O bonds (see Walsh [26]).

We thank Dr. Bernt Klewe for assisting with data collection and for his interest in the problem.

[5/2421 *Received, 12th December*, 1975]

---

[21] K. A. R. Mitchell, *Chem. Rev.*, 1969, **69**, 157.

[22] W. G. Salmond, *Quart. Rev.*, 1968, **22**, 253.

[23] C. A. Coulson, *J. Chem. Soc.*, 1964, 1442.

[24] R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, 1968, 231.

[25] D. G. Nicholson and P. Rademacher, *Acta Chem. Scand.*, 1974, **A28**, 1136.

[26] A. D. Walsh, *J. Chem. Soc.*, 1953, 2260, and the five papers following.