Structural Studies in Main Group Chemistry. Part VIII.[1] The Crystal and Molecular Structure of Bis(*N*-methyl-*N*-acetylhydroxylamino)-dimethyltin(IV)

By **Philip G. Harrison,* Trevor J. King,** and **John A. Richards,** Department of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD

The crystal structure of $Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2$ has been determined by *X*-ray methods. The crystals are monoclinic, space group $P2_1/c$ with $a = 8{\cdot}8933(8)$, $b = 7{\cdot}2861(7)$, $c = 20{\cdot}5352(14)$ Å, $\beta = 104{\cdot}472(5)°$. The geometry at tin is distorted octahedral, the overall symmetry approximating to C_{2v}. The two *N*-acetylhydroxylamine residues function as bidentate ligands forming one short covalent and one long co-ordinate bond to tin, whilst the Me–Sn–Me group is not linear, the C–Sn–C bond angle being 145·8°. Bond distances within the two ligand residues indicate significant multiple-bond character for the C–N bonds and single bond zwitterionic character for the C=O bonds.

BIFUNCTIONAL diorganotin(IV) derivatives possessing potentially bridging or bidentate groups are known to be able to assume either four-co-ordinate tetrahedral or six-co-ordinate octahedral structures, or a structure intermediate between these extremes, depending on the nature of the groups bonded to tin. Thus, whereas diphenyltin dichloride consists of isolated molecules in the solid,[2] both dimethyltin [3] and bis(chloromethyl)tin [4] dichlorides exhibit weak chloride bridging, which leads to stereochemistries at tin which are best described as intermediate between tetrahedral and octahedral. Strong fluoride bridging in dimethyltin difluoride results in octahedral co-ordination at tin and the formation of linear $(SnF_2)_n$ chains with methyl groups above and below the plane of the chain.[5] A similar range of co-ordination is exhibited by potentially bidentate oxygen ligands. Dimethyltin dinitrate [6] and bis(oxinate) [7] have co-ordination polyhedra which may be described as distorted octahedral with *trans*- and *cis*-methyl groups, respectively. Bis(pentane-2,4-dionato)-dimethyltin [8] and bis(fluorosulphato)dimethyltin [9] are regularly octahedral with linear C–Sn–C groupings. In the latter compound, however, the fluorosulphato-ligands bridge adjacent tin atoms, whilst the former compound consists of discrete monomeric units.

As part of our study into derivatives with the M–O–N grouping [1,10,11] and the relationship between spectro-

---

[1] Part VII, P. G. Harrison and T. J. King, *J.C.S. Dalton*, 1974, 2298.

[2] P. T. Green and R. F. Bryan, *J. Chem. Soc.* (*A*), 1971, 549.

[3] A. G. Davies, H. J. Milledge, D. C. Puxley, and R. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2862.

[4] N. G. Bokii, Yu. T. Struchkov, and A. K. Prokof'ev, *J. Strukt. Chem.*, 1972, **13**, 665.

[5] E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, 1966, **8**, 995.

[6] J. Hilton, E. K. Nunn, and S. C. Wallwork, *J.C.S. Dalton*, 1973, 173.

[7] E. O. Schlemper, *Inorg. Chem.*, 1967, **6**, 2012.

[8] G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 1973, **12**, 677.

[9] F. A. Allen, J. A. Lerbscher, and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 2507.

[10] P. G. Harrison, *Inorg. Chem.*, 1973, **12**, 1545.

[11] P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 1970, **9**, 175; P. G. Harrison and J. J. Zuckerman, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 5.

scopic properties and structure,[1,12] we report in this paper the crystal structure of bis(*N*-methyl-*N*-acetylhydroxylamino)dimethyltin(IV).

TABLE 1

Final positional atomic parameters (estimated standard deviations are given in parentheses)

Atom	x/a	y/b	z/c
Sn(1)	0·31857(4)	0·51188(5)	0·38994(2)
O(1)	0·42208(46)	0·65174(61)	0·32250(19)
O(2)	0·57285(44)	0·60496(58)	0·44935(19)
O(3)	0·08973(49)	0·36042(77)	0·40085(21)
O(4)	0·15442(46)	0·51026(57)	0·29482(20)
N(1)	0·56424(50)	0·73262(62)	0·34986(21)
N(2)	0·00811(49)	0·45002(64)	0·29451(23)
C(1)	0·63410(58)	0·70533(72)	0·41286(26)
C(2)	0·78923(77)	0·79095(120)	0·44258(36)
C(3)	0·61412(90)	0·84280(108)	0·30033(34)
C(4)	−0·01821(63)	0·37501(76)	0·34881(28)
C(5)	−0·09831(83)	0·47582(98)	0·22991(39)
C(6)	−0·17790(74)	0·30374(100)	0·34665(39)
C(7)	0·24293(81)	0·72569(99)	0·44295(34)
C(8)	0·41434(74)	0·24515(84)	0·39581(32)

EXPERIMENTAL

Crystals of bis(*N*-methyl-*N*-acetylhydroxylamino)dimethyltin(IV) were prepared by the azeotropic dehydration of a mixture of dimethyltin(IV) oxide and *N*-methyl-*N*-acetylhydroxylamine in a 1 : 2 ratio in boiling benzene, followed by recrystallisation from diethyl ether.[13] A suitable crystal of dimensions *ca.* 0·8 × 0·6 × 0·5 mm was mounted directly onto a fine glass fibre, and used to obtain the preliminary cell data and subsequent intensity measurements.

TABLE 3

Bond distances with standard deviations

Bonded atoms	Bond length (Å)	Bonded atoms	Bond length (Å)
Sn(1)–C(7)	2·105(8)	Sn(1)–O(4)	2·126(4)
Sn(1)–C(8)	2·113(6)	Sn(1)–O(3)	2·374(5)
Sn(1)–O(1)	2·107(4)	Sn(1)–O(2)	2·384(4)
N(1)–O(1)	1·331(6)	C(1)–O(2)	1·264(7)
N(1)–O(3)	1·450(9)	C(1)–C(2)	1·498(8)
N(1)–C(1)	1·303(6)		
N(2)–O(4)	1·372(6)	C(4)–O(3)	1·250(6)
N(2)–C(5)	1·436(8)	C(4)–C(6)	1·502(9)
N(2)–C(4)	1·314(8)		

Crystal Data.—$C_8H_{18}O_4N_2Sn$, M = 324·93, space group $P2_1/c$, a = 8·8933(8), b = 7·2861(7), c = 20·5352(14) Å, β = 104·472(5)°, U = 1288·4 Å^3, D_m = 1·66 (by flotation), Z = 4, D_c = 1·675, $F(000)$ = 648.

The space group was uniquely determined as $P2_1/c$ by the systematic absences $h0l$ for $l = 2n + l$ and $0k0$ for $k = 2n + l$ from zero and first layer equi-inclination Weissenberg photographs. Intensity data up to θ = 29·99° were collected using Mo-K_α radiation (λ = 0·71069 Å) on a Hilger-Watt four-circle diffractometer. Accurate cell parameters were obtained by least-squares refinement using *ca.* 25 reflections. Each reflection was counted for 30 s and the associated two background counts for 10 s. The reflections were brought to the same relative intensities by reference reflections taken for every 100 reflections recorded; the diffractometer was referenced every 200 reflections recorded. The background counts were low and were included in the usual manner. Intensities varied from 1 to 7·85 × 10^5. All reflections with a corrected intensity less than 2·5 times the estimated standard deviation of the total counts were considered as non-observed and were not used, reducing the total number of the reflections from 3756 to 2710. The number of reflections was further reduced to 2178 by elimination of the lower intensity reflections, to enable adequate computer storage for refinement. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

TABLE 2

Final anisotropic thermal parameters * (estimated standard deviations are given in parentheses)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	4·23(2)	5·44(2)	3·93(2)	−0·75(2)	0·71(1)	0·18(2)
O(1)	5·41(22)	7·72(26)	3·96(19)	2·34(20)	0·41(16)	−0·45(18)
O(2)	4·82(20)	6·90(25)	4·25(19)	1·62(18)	0·72(15)	−0·92(17)
O(3)	5·08(23)	10·99(37)	4·94(23)	−2·45(23)	0·52(18)	1·62(23)
O(4)	4·45(18)	8·22(29)	4·34(18)	1·85(19)	0·32(15)	−0·47(18)
N(1)	4·75(23)	5·21(24)	4·27(21)	1·22(19)	1·07(18)	−0·25(18)
N(2)	3·84(21)	5·01(22)	5·07(24)	−0·68(17)	0·04(18)	−0·03(19)
C(1)	4·02(24)	4·97(26)	4·80(27)	0·90(20)	1·06(20)	0·35(21)
C(2)	5·78(38)	11·15(57)	6·48(40)	4·57(39)	−0·09(30)	−1·26(38)
C(3)	8·89(50)	8·77(49)	5·53(36)	3·80(40)	1·43(33)	−1·54(32)
C(4)	4·63(28)	4·86(27)	5·39(31)	−0·68(22)	0·85(23)	−0·46(23)
C(5)	5·79(35)	8·26(46)	6·64(39)	−1·69(32)	−1·48(29)	1·73(33)
C(6)	4·61(31)	7·47(41)	8·94(49)	−1·60(29)	1·74(31)	0·20(35)
C(7)	6·57(38)	7·32(40)	6·01(36)	−1·34(31)	1·55(29)	0·13(30)
C(8)	6·37(36)	5·58(33)	5·68(33)	−0·25(27)	0·81(27)	−0·62(26)

* U_{ij} values as listed have been multiplied by 100.

Structure Determination and Refinement.—The positional parameters of the tin atom in the asymmetric unit were obtained from a Patterson synthesis $P(uvw)$, and these were used to phase the initial structure factor calculation resulting in an R value of 0·81. A Fourier synthesis employing the rejection test ($F_o \times 0{\cdot}25 - F_c$) $\geqslant 0$ produced 29 unique peaks where the value of the function at any point was >35. The majority of these peaks were not chemically acceptable and were rejected save for six peaks situated within acceptable bonding distance of the tin atom. Four cycles of isotropic full-matrix least-squares refinement failed to produce a satisfactory subsequent Fourier synthesis, convergence being obtained at R = 0·272. Examination of positional and isotropic thermal parameters resulted in the rejection of two further peaks.

---

[12] P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S., Dalton*, 1974, 1723.

[13] P. G. Harrison and J. A. Richards, manuscript in preparation.

Two cycles of isotropic full-matrix refinement and subsequent Fourier synthesis with rejection conditions as before using the tin and the four remaining light atom positions (using carbon scattering factors) reduced the R-value to 0·226 and produced 17 unique peaks with a maximum value of $\geqslant 35{\cdot}0$, 14 of which gave a chemically acceptable model. Atom types were ascribed to the peaks and two cycles of isotropic full-matrix followed by two cycles of anisotropic block-diagonal least-squares refinement reduced the R-value to 0·051. The weighting scheme $w = 1/\{1 + (F_o - 6{\cdot}00)/24{\cdot}0)^2\}$ was then introduced, and two further cycles of block and two of full-matrix anisotropic least-squares refinement yielded an R-value of 0·048. At this stage 34 reflections with $F_c > 1/4\ F_o$ were discarded, and two cycles of anisotropic full-matrix refinement failed to reduce the R-value although the atomic parameters continued to settle. Rejection of a further 27 reflections using the same rejection conditions produced a final R-value of 0·045 with the shift/error ratio for all positional and thermal parameters being $\not> 0{\cdot}003$. A difference Fourier synthesis indicated negligible residual electron density. The scattering factors used were those for neutral atoms.

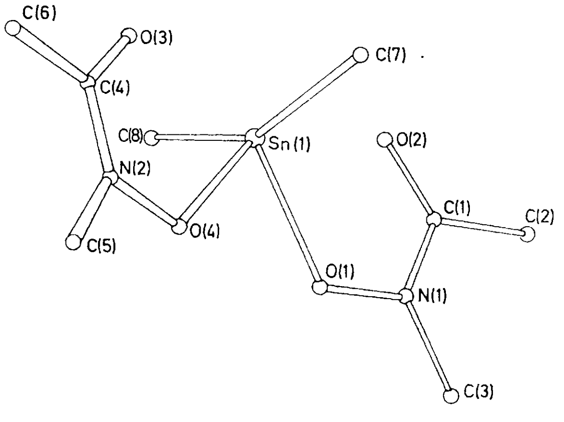
TABLE 4

Bond angles with standard deviations

Atoms defining angle	Bond angle (°)	Atoms defining angle	Bond angle (°)
(*a*) With central tin atom			
C(8)–Sn(1)–C(7)	145·84(26)	O(3)–Sn(1)–O(2)	144·07(14)
O(4)–Sn(1)–O(1)	73·22(15)	O(3)–Sn(1)–C(8)	84·83(23)
O(4)–Sn(1)–C(7)	104·15(21)	O(3)–Sn(1)–C(7)	84·43(24)
O(4)–Sn(1)–C(8)	102·81(20)	O(2)–Sn(1)–O(1)	71·61(14)
O(1)–Sn(1)–C(7)	103·33(24)	O(2)–Sn(1)–C(8)	72·16(19)
O(1)–Sn(1)–C(8)	104·25(23)	O(2)–Sn(1)–C(7)	74·10(20)
O(3)–Sn(1)–O(4)	71·11(15)		
(*b*) Within the ligands			
Sn(1)–O(4)–N(2)	116·02(32)	C(5)–N(2)–C(4)	128·46(51)
Sn(1)–O(3)–C(4)	111·91(41)	O(3)–C(4)–N(2)	119·95(53)
O(4)–N(2)–C(5)	111·57(50)	O(3)–C(4)–C(6)	120·95(58)
O(4)–N(2)–C(4)	119·93(40)	C(6)–C(4)–N(2)	119·09(48)
Sn(1)–O(1)–N(1)	116·42(29)	O(1)–N(1)–C(3)	111·13(41)
Sn(1)–O(2)–C(1)	110·82(29)	O(1)–N(1)–C(1)	119·99(46)
C(3)–N(1)–C(1)	128·88(48)	O(2)–C(1)–C(2)	119·27(48)
O(2)–C(1)–N(1)	120·52(45)	C(2)–C(1)–N(1)	120·20(54)

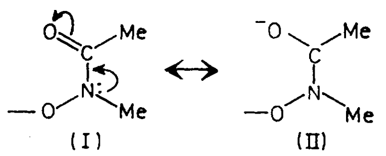
RESULTS AND DISCUSSION

The structure and atomic numbering scheme for bis(N-methyl-N-acetylhydroxylamino)dimethyltin(IV) is depicted in the Figure. The geometry at tin is that of a distorted octahedron, the overall symmetry of the molecule approximating to C_{2v}. The Me–Sn–Me group deviates significantly from linearity (C–Sn–C = 145·8°), with the Sn–C bond distances falling within the range observed for similar derivatives (Table 7). The two anisobidentate hydroxylamino-residues are almost equivalent and form two heterocyclic $\overline{\mathrm{Sn{\leftarrow}O{:}C{\cdot}N{\cdot}O}}$ rings which are each essentially planar, but are inclined at an angle of 9° with respect to each other. The rings both contain one short covalent Sn–O bond (2·107, 2·126 Å) and one longer co-ordinate bond (2·374, 2·384 Å), these distances being very similar to those observed for the analogous bonds in $\mathrm{Ph_3Sn{\cdot}O{\cdot}NPh{\cdot}COPh}$,[1] and demonstrate that the distortion from regular octahedral co-ordination results from the steric demands of the ligands. The co-ordination at tin thus resembles very closely that in dimethyltin dinitrate [6] and dimethyltin bis(dimethyldithiocarbamate).[14]



Atomic numbering in $\mathrm{Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2}$

As in $\mathrm{Ph_3Sn{\cdot}O{\cdot}NPh{\cdot}COPh}$,[1] the bond distances of the N-acetylhydroxylamine residue are consistent with a significant contribution of the zwitterionic canonical form (II) to the electronic distribution. Ligand bond distances for $\mathrm{Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2}$, $\mathrm{Ph_3Sn{\cdot}O{\cdot}NPh{\cdot}COPh}$, and $\mathrm{HO{\cdot}NH{\cdot}CO{\cdot}Me{\cdot}\frac{1}{2}H_2O}$ [15] are compared in Table 6 and are not unexpectedly very similar. The two C=O bond distances in $\mathrm{Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2}$ differ slightly (1·250, 1·264 Å), but both are longer than that generally found in simple carbonyl compounds such as esters, aldehydes, and ketones (1·23 Å),[16] and compare with the distances found in zwitterionic compounds such as DL-serine (1·26 Å). The endocyclic C–N bond distances (1·303, 1·314 Å) are significantly shorter than the normal single-bond values found for the exocyclic C–N bonds (1·450, 1·436 Å), but are longer than C=N bond distances found in hydroximate derivatives (1·26—1·29 Å).[17,18] The N–O bond distances in the two tin derivatives are slightly shorter than in $\mathrm{HONH{\cdot}COMe{\cdot}\frac{1}{2}H_2O}$,[15] but this difference is attributable



---

[14] T. Kimura, N. Yasuoka, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Japan*, 1972, **45**, 1649.

[15] B. H. Bracher and R. W. H. Small, *Acta Cryst.*, 1970, **B26**, 1705.

[16] 'Molecular Structures and Dimensions,' Vol. A1, eds. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town, N.V.A. Oosthoek's Vitgevers Mij Utrecht, 1972.

[17] I. K. Larsen, *Acta Chem. Scand.*, 1971, **25**, 2409.

[18] M. G. Waite and G. A. Sim, *J. Chem. Soc.* (*B*), 1971, 752; 1102.

TABLE 5

Weighted least-squares equations ($w = z$) in their normal form of the mean planes through groups of atoms and deviations of the atoms from these planes (in Å) *

(a) Equation: $pI + qJ + rK = s$, where I, J, K are orthogonal co-ordinates in Å, related to the monoclinic co-ordinates in the following way: $I = X + Z \cos\beta$; $J = Y$; $K = Z \sin\beta$.

Plane	p	q	r	s
(1) C(8), C(7), Sn(1)	0·8931	0·3909	0·2227	3·92757
(2) O(4), O(3), N(2), C(6), C(5), C(4), Sn(1)	−0·3652	0·8896	0·2743	5·0510
(3) O(2), O(1), N(1), C(1), C(2), C(3), Sn(1)	−0·5072	0·8229	0·2563	4·5567
(4) O(4), O(3), O(2), O(1)' Sn(1)	−0·4410	0·8681	0·2279	4·6412
(5) O(4), O(1), Sn(1)	−0·4529	0·8621	0·2273	4·6009
(6) C(1), N(1), O(1)	−0·5433	0·7995	0·2562	4·2992
(7) C(4), N(2), O(4)	−0·3055	0·9001	0·3106	5·2100
(8) C(2), C(1), O(2)	−0·5358	0·8011	0·2670	4·4219
(9) C(3), N(1), O(1)	−0·5448	0·7962	0·2631	4·3245
(10) C(6), C(4), O(3)	−0·3365	0·8869	0·3165	5·2753
(11) C(5), N(2), O(4)	−0·3083	0·9089	0·2807	5·0675
(12) O(2), O(1), Sn(1)	−0·4433	0·8642	0·2380	4·6999
(13) O(4), O(3), Sn(1)	−0·4375	0·8721	0·2193	4·5890
(14) O(3), O(2), Sn(1)	−0·4368	0·8714	0·2233	4·6179
(15) N(2), O(3), C(6)	−0·3314	0·8932	0·3040	5·1858

(b) Deviations from the planes

Plane (2)		Plane (3)		Plane (4)		Plane (2)		Plane (3)		Plane (4)	
Atom	Δ	Atom	Δ	Atom	Δ	Atom	Δ	Atom	Δ	Atom	Δ
O(4)	−0·08496	O(2)	−0·05396	O(4)	−0·01610	C(4)	−0·00533	C(3)	0·03858	C(7) *	2·00594
O(3)	−0·06918	O(1)	−0·07007	O(3)	0·01040	Sn(1)	0·08936	Sn(1)	0·07748	C(8) *	−2·02603
N(2)	−0·00249	N(1)	−0·01570	O(2)	−0·00811	C(7) *	2·10932	C(7) *	2·10864		
C(6)	0·03554	C(1)	−0·00939	O(1)	0·01709	C(8) *	−1·90758	C(8) *	−1·90845		
C(5)	0·03706	C(2)	0·03307	Sn(1)	−0·00327						

The atoms marked by asterisks do not determine the planes.

(c) Angles between the planes (°)

	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)
(1)	85·26	85·75	89·79	89·03	83·36	81·47	83·92	83·30	83·30	81·81	89·71	89·94	89·98	83·05
(2)		9·06	5·24	5·92	11·50	4·05	11·03	11·64	2·93	3·46	5·14	5·30	5·14	2·59
(3)			4·87	4·18	2·46	12·79	2·15	2·67	11·01	12·52	4·48	5·33	5·25	11·20
(4)				0·77	7·24	9·29	7·02	7·51	7·93	8·52	0·63	0·58	0·41	7·78
(5)					6·51	9·96	6·32	6·80	8·53	9·24	0·83	1·15	1·09	8·43
(6)						15·16	0·76	0·45	13·35	14·95	6·91	7·65	7·60	13·58
(7)							14·62	15·24	1·96	1·79	9·17	9·34	9·19	1·58
(8)								0·63	12·78	14·48	6·63	7·47	7·40	13·05
(9)									13·40	15·09	7·15	7·94	7·88	13·67
(10)										2·90	7·71	8·08	7·90	0·85
(11)											8·51	8·47	8·35	2·08
(12)												1·21	1·01	7·63
(13)													0·23	7·88
(14)														7·71

* According to V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

TABLE 6

Comparison of bond distances in $Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2$, $Ph_3SnO{\cdot}NPh{\cdot}COPh$, and $HO{\cdot}NH{\cdot}COMe{\cdot}\frac{1}{2}H_2O$

Bond	$Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2$	$Ph_3SnO{\cdot}NPh{\cdot}COPh$ [1]	$HO{\cdot}NH{\cdot}COMe{\cdot}\frac{1}{2}H_2O$ [15]
N–O	1·381(6), 1·372(6)	1·384(6)	1·400(5)
C(=O)–N	1·303(6), 1·314(8)	1·304(9)	1·333(6)
C=O	1·264(7), 1·250(6)	1·265(9)	1·245(6)
C–R	1·498(8), 1·502(9) [a]	1·495(7) [b]	1·505(6) [a]
N–C(R)	1·450(9), 1·436(8) [a]	1·430(10) [b]	—

[a] R = Me. [b] R = Ph

TABLE 7

Comparison of bond parameters of $Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2$ with those in related compounds

Compound	Geometry at tin	$C\widehat{Sn}C$ (°)	r(Sn–C)(Å)	r(Sn–O)(Å)	r(Sn · · · O) (Å)	Ref.
$Me_2Sn(O{\cdot}NMe{\cdot}COMe)_2$	Distorted octahedral	145·8(3)	2·105(8) 2·113(6)	2·107(4) 2·126(4)	2·374(5) 2·384(4)	This work
$Ph_3Sn{\cdot}O{\cdot}NPh{\cdot}COPh$	Trigonal bipyramidal	—	*eq* 2·136(8), *ax* 2·176(9)	2·091(5)	2·308(4)	*a*
$Me_2Sn(oxin)_2$	Distorted octahedral	110·7	2·15(2) 2·17(2)	2·11(1) 2·10(1)		*b*
$Me_2Sn(NO_3)_2$	Distorted octahedral	143·6(8)	2·11(2), 2·12(2)	2·15(1), 2·17(1)	2·70(2), 2·42(1)	*c*
$Me_2Sn(salen)$	Distorted octahedral	161(1)	2·07, 2·15	2·21		*d*
$Me_2Sn(acac)_2$	Octahedral	180	2·14(2)	2·18(1)	2·20(1)	*e*
$Me_2Sn(SO_3F)_2$	Octahedral	180	2·081(9)	2·240(6)	2·248(7)	*f*
$Me_2SnCl_2{\cdot}2DMSO$	Octahedral	180	2·07(6) 2·08(5)		2·32(3) 2·38(3)	*g*
$Me_2SnCl_2{\cdot}2pyNO$	Octahedral	180	2·225(25)		2·251(16)	*h*

[a] Ref. 1. [b] Ref. 7. [c] Ref. 6. [d] M. Calligaris, G. Nardin, and L. Randaccio, *J.C.S. Dalton*, 1972, 2003. [e] Ref. 9. [f] Ref. 9. [g] N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1970, 1257. [h] E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc.* (*A*), 1969, 913.

to lack of substitution at nitrogen and hydrogen bonding present in the latter compound, rather than gross electronic redistributions.

We thank the S.R.C. for the award of an INSTANT Studentship (to J. A. R.).

[4/776 *Received, 17th April, 1974*]