# Structural Studies in Main-Group Chemistry. Part XVI.[1] Crystal and Molecular Structures of Bis(*N*-acetylhydroxylamino)dimethyltin(IV) and Its Monohydrate

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The crystal structures of $Me_2Sn(ONH{\cdot}COMe)_2$ (I) and its monohydrate (II) have been determined from diffractometer data by Patterson and Fourier techniques and refined by least-squares techniques to final *R* values of 0.063 [(I), 1 342 independent non-zero observed reflections] and 0 048 [(II), 2 183 reflections], respectively. Crystals of (I) are monoclinic, space group *C*2/*c*, with *a* = 13.791 8(7), *b* = 8.680 3(5), *c* = 13.468 0(7) Å, β = 139.53(5)°; crystals of (II) are also monoclinic, space group $P2_1/c$, with *a* = 14.110 7(7), *b* = 20.014 6(11), *c* = 8.863 6(5) Å, β = 106.95(4)°. The asymmetric unit of (II) contains two crystallographically independent $Me_2Sn(ONH{\cdot}COMe)_2$ molecules, which have almost identical geometries, but differ significantly from the geometry of the $Me_2Sn(ONH{\cdot}COMe)_2$ molecule in the anhydrous material, in which the tin atom lies on a crystallographic two-fold axis of symmetry. In all three molecules, the tin atom is six-co-ordinated by two chelating *N*-acetylhydroxylamino-ligands and two methyl groups, but, whereas the two methyl groups in (II) occupy essentially *cis*-positions of a distorted octahedron about tin [C–Sn–C 109.1(4)°; Sn–C 2.144(6), Sn–O 2.106(4), Sn···O 2.228(4) Å], the two molecules of $Me_2Sn(ONH{\cdot}COMe)_2$ in (II) have geometries intermediate between ideal *cis*- and *trans*-octahedral [C–Sn–C 156.8(7)°; Sn–C 2.17(2), Sn–O 2.16(2), Sn···O 2.36(2), 2.45(2) Å]. In the crystal lattice of (I), neighbouring molecules are held together by two NH···O=C hydrogen bonds connecting adjacent *N*-hydroxylamino-groups giving rise to infinite linear stacks, with no significant bonding interactions between neighbouring stacks. The crystal lattice of (II) is made up of alternate layers, each composed of the two crystallographically distinct $Me_2Sn(ONH{\cdot}COMe)_2$ molecules and separated by layers of water molecules, which connect the layers of $Me_2Sn(ONH{\cdot}COMe)_2$ molecules by a network of hydrogen bonds. $Me_2Sn(ONH{\cdot}COMe)_2$ molecules within each layer are also held together by hydrogen bonds, although in this case between NH and an oxygen atom bonded directly to the tin atom of an adjacent molecule.

WE have previously determined the crystal and molecular structure of $Me_2Sn(ONMe{\cdot}COMe)_2$, which consists of discrete molecules in the solid.[2] $Me_2Sn(ONH{\cdot}COMe)_2$ (I), on the other hand, forms a monohydrate (II) in addition to the anhydrous material, and both compounds exhibit characteristics indicative of intermolecular association in the solid (infusibility, insolubility, a slow decrease in the tin-119m Mössbauer recoil-free fraction with increase in temperature). We now report the results of *X*-ray studies of both compounds in order to elucidate the nature of the intermolecular binding in the solid.

## EXPERIMENTAL

$Me_2Sn(ONH{\cdot}COMe)_2$ (I) was prepared by the azeotropic dehydration of dimethyltin oxide and two moles of *N*-acetylhydroxylamine in benzene. Recrystallisation of the amorphous powder obtained from methanol under scrupulously anhydrous conditions afforded crystals of anhydrous $Me_2Sn(ONH{\cdot}COMe)_2$, (I) whilst aerobic recrystallisation gave crystals of the monohydrate (II). Crystals of dimensions 0.3 × 0.3 × 0.4 mm (I) and 0.3 × 0.4 × 0.4 mm (II) were mounted directly on fine glass fibres and used for the collection of cell and intensity data.

*Structural Determination of the Hydrate* (II).—*Crystal data*. $C_6H_{16}N_2O_5Sn$, *M* = 314.84, *a* = 14.1 107(7), *b* = 20.014 6(11), *c* = 8.863 6(5) Å, β = 106.95(4)°, *U* = 2 394.58 Å$^3$, *Z* = 8, *F*(000) = 1 248. Mo-$K_\alpha$ radiation, λ = 0.710 69 Å; μ(Mo-$K_\alpha$) = 22.08 cm$^{-1}$. Space group $P2_1/c$ from systematic absences *h*0*l* for $l = 2n + 1$ and 0*k*0 for $k = 2n + 1$.

The space group was determined from oscillation and Weissenberg photographs. The intensities of 5 950 independent reflections were measured by use of a Hilger and Watts Y 290 four-circle diffractometer. Only the 2 183 reflections with $I > 3.0\sigma(I)$ were used for the structure determination and refinement made with the '*X*-ray '70' suite of programmes. Corrections to the intensities were made for Lorentz and polarisation effects, but none were made for absorption since the value of μ was low.

TABLE 1

Final fractional atomic co-ordinates for (II), with estimated standard deviations in parentheses

| Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Sn(1) | 0.981 88(12) | 0.103 81(9) | 0.389 69(19) |
| Sn(2) | 0.485 10(11) | 0.395 97(9) | 0.386 13(18) |
| O(1) | 0.978 5(13) | 0.202 4(7) | 0.292 6(16) |
| O(2) | 0.891 8(12) | 0.097 9(8) | 0.118 4(16) |
| O(3) | 0.046 2(11) | 0.042 7(7) | 0.638 0(16) |
| O(4) | 1.043 8(12) | 0.173 5(7) | 0.576 8(16) |
| O(5) | 0.458 5(12) | 0.299 0(7) | 0.272 7(17) |
| O(6) | 0.569 8(13) | 0.391 5(8) | 0.192 7(18) |
| O(7) | 0.443 1(11) | 0.463 4(7) | 0.585 0(16) |
| O(8) | 0.408 5(12) | 0.333 7(7) | 0.511 2(17) |
| O(9) | 0.287 8(11) | 0.230 3(7) | 0.264 3(16) |
| O(10) | 1.173 9(11) | 0.256 6(7) | 0.459 0(17) |
| C(1) | 1.117 0(17) | 0.070 2(12) | 0.345 2(28) |
| C(2) | 0.834 9(16) | 0.094 6(12) | 0.417 5(27) |
| C(3) | 0.901 9(17) | 0.151 2(13) | 0.046 6(26) |
| C(4) | 0.861 3(21) | 0.156 0(15) | −0.130 6(28) |
| C(5) | 1.089 2(17) | 0.081 0(11) | 0.748 1(24) |
| C(6) | 1.140 7(20) | 0.056 9(12) | 0.914 6(26) |
| C(7) | 0.359 3(19) | 0.445 8(12) | 0.227 6(26) |
| C(8) | 0.632 0(18) | 0.386 0(13) | 0.540 8(28) |
| C(9) | 0.556 4(20) | 0.338 7(13) | 0.117 5(27) |
| C(10) | 0.601 1(22) | 0.326 6(14) | −0.017 4(30) |
| C(11) | 0.397 7(15) | 0.429 1(11) | 0.661 2(23) |
| C(12) | 0.359 3(20) | 0.458 6(12) | 0.788 6(28) |
| N(1) | 0.941 5(16) | 0.205 2(10) | 0.126 8(23) |
| N(2) | 1.090 4(15) | 0.145 8(9) | 0.723 1(20) |
| N(3) | 0.495 0(14) | 0.290 5(9) | 0.147 7(20) |
| N(4) | 0.376 9(14) | 0.366 0(9) | 0.625 7(20) |

A Patterson synthesis was used to determine the positional parameters of the two tin atoms in the asymmetric unit, and these were used to phase the initial structure-factor calculation. Isotropic full-matrix refinement followed by anisotropic full-matrix refinement gave a final *R*

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[1] Part XV, P. F. R. Ewings, P. G. Harrison, and A. Mangia, *J. Organometallic Chem.*, 1976, **114**, 35.

[2] P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1975, 826.

of 0.048. No weighting scheme was applied. Attempts to locate the hydrogen atoms were unsuccessful.

Final fractional atomic co-ordinates are listed in Table 1, and intramolecular bond distances and angles, and hydrogen bond distances in Table 2. Least-squares planes data are given in Table 3. Observed and calculated structure factors and anisotropic thermal parameters for both compounds are listed in Supplementary Publication No. SUP 21809 (25 pp., 1 microfiche).*

TABLE 2

Intramolecular bond distances (Å) and angles (°) in (II), with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Bond distances | | | |
| (i) Molecule (1) | | | |
| Sn(1)–O(1) | 2.15(1) | Sn(1)–O(3) | 2.49(1) |
| Sn(1)–O(4) | 2.15(1) | Sn(1)–C(1) | 2.16(2) |
| Sn(1)–O(2) | 2.35(1) | Sn(1)–C(2) | 2.17(2) |
| N(1)–O(1) | 1.41(2) | C(3)–C(4) | 1.51(3) |
| N(1)–C(3) | 1.33(3) | C(3)–O(2) | 1.25(3) |
| N(2)–O(4) | 1.39(2) | C(5)–C(6) | 1.52(3) |
| N(2)–C(5) | $1.31_5$(3) | C(5)–O(3) | 1.25(2) |
| (ii) Molecule (2) | | | |
| Sn(2)–O(5) | 2.17(1) | Sn(2)–O(7) | 1.43(1) |
| Sn(2)–O(8) | 2.16(2) | Sn(2)–C(7) | 2.16(2) |
| Sn(2)–O(6) | 2.36(2) | Sn(2)–C(8) | 2.14(2) |
| N(3)–O(5) | 1.36(3) | C(9)–C(10) | 1.52(3) |
| N(3)–C(9) | 1.38(4) | C(9)–O(6) | 1.23(4) |
| N(4)–O(8) | 1.38(3) | C(11)–C(12) | 1.51(3) |
| N(4)–C(11) | 1.31(3) | C(11)–O(7) | 1.26(3) |
| (ii) Hydrogen bonds | | | |
| O(10) · · · O(9′) | 2.73(2) | O(10) · · · O(9) | 2.73(3) |
| O(10) · · · O(4) | 2.89(2) | O(10) · · · N(2″) | 2.85(2) |
| O(9) · · · O(5) | $2.75_5$(2) | O(9) · · · N(4″) | 2.78(3) |
| O(8) · · · N(3′) | 2.87(2) | O(4) · · · N(1′) | 2.92(2) |
| (*b*) Angles | | | |
| (i) Molecule (1) | | | |
| C(1)–Sn(1)–C(2) | 156.7(7) | O(2)–Sn(1)–C(1) | 90.3(6) |
| O(1)–Sn(1)–O(4) | 70.6(4) | O(2)–Sn(1)–C(2) | 84.3(5) |
| O(1)–Sn(1)–C(1) | 97.4(6) | O(2)–Sn(1)–O(3) | 146.9(4) |
| O(1)–Sn(1)–C(2) | 102.4(6) | O(3)–Sn(1)–O(4) | 70.7(4) |
| O(4)–Sn(1)–C(1) | 99.2(6) | O(3)–Sn(1)–C(1) | 83.9(6) |
| O(4)–Sn(1)–C(2) | 89.9(6) | O(3)–Sn(1)–C(2) | 88.4(5) |
| O(2)–Sn(1)–O(1) | 72.1(4) | | |
| Sn(1)–O(1)–N(1) | 114.4(9) | Sn(1)–O(4)–N(2) | 115.9(9) |
| Sn(1)–O(2)–C(3) | 113.2(10) | Sn(1)–O(3)–C(5) | 111.4(10) |
| O(1)–N(1)–C(3) | 119.7(14) | O(4)–N(2)–C(5) | 121.0(13) |
| N(1)–C(3)–O(2) | 119.8(20) | N(2)–C(5)–O(3) | 119.9(18) |
| N(1)–C(3)–C(4) | 118.5(16) | N(2)–C(5)–C(6) | 116.8(19) |
| O(2)–C(3)–C(4) | 120.9(16) | O(3)–C(5)–C(6) | 123.3(16) |
| (ii) Molecule (2) | | | |
| O(7)–Sn(2)–C(8) | 156.9(8) | O(6)–Sn(2)–C(8) | 81.9(7) |
| O(5)–Sn(2)–O(8) | 71.1(4) | O(6)–Sn(2)–C(7) | 92.1(7) |
| O(5)–Sn(2)–C(8) | 102.6(6) | O(7)–Sn(2)–O(6) | 146.2(4) |
| O(5)–Sn(2)–C(7) | 96.5(6) | O(7)–Sn(2)–O(8) | 71.5(4) |
| O(8)–Sn(2)–C(8) | 98.9(6) | O(7)–Sn(2)–C(8) | 89.0(6) |
| O(8)–Sn(2)–C(7) | 99.4(7) | O(7)–Sn(2)–C(7) | 83.6(6) |
| O(6)–Sn(2)–O(5) | 71.7(5) | | |
| Sn(2)–O(5)–N(3) | 115.8(10) | Sn(2)–O(8)–N(4) | 115.1(10) |
| Sn(2)–N(3)–C(9) | 113.3(14) | Sn(2)–O(7)–C(11) | 110.7(10) |
| O(5)–N(3)–C(9) | 118.7(15) | O(8)–N(4)–C(11) | 121.9(17) |
| N(3)–C(9)–O(6) | 120.1(20) | N(4)–C(11)–O(7) | 120.6(18) |
| N(3)–C(9)–C(10) | 118.1(18) | N(4)–C(11)–C(12) | 116.8(18) |
| O(6)–C(9)–C(10) | 121.7(20) | O(7)–C(11)–C(12) | 122.5(17) |
| O(4)–O(10)–O(9) | 132.1(6) | O(5)–O(9)–O(10) | 123.9(6) |
| O(4)–O(10)–O(9′) | 87.1(5) | O(5)–O(9)–O(10′) | 103.7(6) |
| O(4)–O(10)–N(2″) | 119.2(6) | O(5)–O(9)–N(4″) | 82.0(6) |
| O(9)–O(10)–O(9′) | 111.1(6) | O(10)–O(9)–O(10′) | 108.9(6) |
| Sn(1)–O(4)–O(10) | 104.7(5) | Sn(2)–O(5)–O(9) | 119.4(7) |

Single-primed atoms are at *x*, $\frac{1}{2} - y$, $\frac{1}{2} + z$, double-primed atoms at *x*, $\frac{1}{2} - y$, $z - \frac{1}{2}$.

*Structural Determination of* $Me_2Sn(ONH{\cdot}COMe)_2$ (I).—*Crystal data.* $C_6H_{14}N_2O_4Sn$, $M = 296.82$, $a = 13.791\,8(7)$, $b = 8.680\,3(5)$, $c = 13.468\,0(7)$, Å, $\beta = 139.53(5)°$, $U = 1\,037.89$ Å$^3$, $Z = 4$, $F(000) = 536$. Mo-$K_\alpha$ radiation, $\mu$(Mo-$K_\alpha$) = 24.6 cm$^{-1}$. Space group $C2/c$ from systematic absences $hkl$ for $h + k = 2n$, $h0l$ for $l = 2n$ ($h = 2n$), and $0k0$ for $k = 2n$.

The space group determination, intensity data collection, and solution and refinement of the structure were carried

TABLE 3

Weighted least-squares equations in their normal form of the mean planes of (II) and deviations (Å) of atoms from the planes *. Equations are in the form $pI + qJ + rK = s$, where $I$, $J$, $K$ are orthogonal co-ordinates in Å, related to the monoclinic co-ordinates by: $I = X + Z\cos\beta$; $J = Y$, and $K = Z\sin\beta$

Plane (1): Sn(1), O(2), C(3), C(4), N(1), O(1)

$$0.969\,03I - 0.214\,00J - 0.123\,24K = 11.526\,81$$

[Sn(1) 0.072 75, O(2) −0.084 94, C(3) 0.005 71, C(4) 0.048 28, N(1) 0.018 47, O(1) −0.048 86]

Plane (2): Sn(1), O(4), C(5), C(6), N(2), O(3)

$$0.972\,44I - 0.084\,37J - 0.215\,12K = 11.573\,15$$

[Sn(1) 0.042 60, O(4) −0.034 90, C(5) 0.000 33, C(6) 0.025 14, N(2) 0.015 23, O(3) −0.048 40]

Plane (3): Sn(2), O(5), C(9), C(10), N(3), O(6)

$$0.643\,41I - 0.370\,74J + 0.658\,28K = 2.845\,77$$

[Sn(2) −0.027 48, O(5) 0.044 56, C(9) −0.006 45, C(10) 0.016 18, N(3) −0.045 23, O(6) 0.018 43]

Plane (4): Sn(2), O(7), C(11), C(12), N(4), O(8)

$$0.702\,12I - 0.243\,84J + 0.669\,00K = 4.374\,97$$

[Sn(2) −0.013 94, O(7) 0.008 03, C(11) 0.019 25, C(12) −0.012 40, N(4) −0.014 76, O(8) 0.013 82]

Angles (°) between the planes: (1)–(2) 9.11, (3)–(4) 9.09

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

TABLE 4

Final fractional atomic co-ordinates for (I), with estimated standard deviations in parentheses

| Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Sn | 0 | 0.034 63(4) | 0.250 00 |
| C(1) | −0.039 9(8) | 0.177 8(8) | 0.092 0(8) |
| C(2) | 0.129 6(5) | −0.243 5(5) | 0.253 1(4) |
| C(3) | 0.148 2(7) | −0.402 5(7) | 0.227 3(6) |
| O(1) | 0.225 0(5) | −0.032 9(4) | 0.411 9(5) |
| O(2) | 0.005 0(4) | −0.172 7(5) | 0.149 9(4) |
| N | 0.241 9(3) | −0.175 6(4) | 0.384 6(3) |

TABLE 5

Intramolecular bond distances (Å) and angles (°) in (I), with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| (*a*) Bond distances | | | |
| Sn–C(1) | 2.144(6) | O(2)–N | 1.362(5) |
| Sn–O(1) | 2.106(4) | N–O(2) | 1.307(5) |
| Sn–O(2) | 2.228(4) | O(2)–O(3) | 1.492(7) |
| | | O(3)–C(2) | 1.277(6) |
| (*b*) Angles | | | |
| O(1)–Sn(O1′) | 109.1(4) | Sn–O(1)–N | 113.2(3) |
| O(1)–Sn–(O1′) | 147.7(2) | O(1)–N–O(2) | 120.4(4) |
| O(2)–Sn–O(2′) | 75.8(2) | Sn–O(2)–C(2) | 110.9(3) |
| O(1)–Sn–O(1) | 81.5(1) | O(2)–O(2)–C(3) | 121.3(4) |
| C(1)–Sn–O(1) | 104.6(2) | N–C(2)–O(3) | 119.7(4) |
| C(1′)–Sn–O(1) | 94.0(2) | | |
| C(1)–Sn–O(2) | 160.7(2) | | |
| C(1′)–Sn–O(2) | 88.3(2) | | |

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

out as for (II) using 1 342 independent reflections with $I > 6.5\sigma(I)$ employing the CRYSTALS suite of programmes. However, before the final cycle of anisotropic least-squares refinement, the weighting scheme $w = [1 + (F_o - P_2)/P_1]^{-2}$, where $P_1 = P_2 = 14.0$, was applied, giving $R$ 0.063.

Final fractional atomic co-ordinates are listed in Table 4, and intramolecular bond distances and angles in Table 5. The scattering factors used were those for neutral atoms.[3]

## DISCUSSION

Several tin compounds are known to form both anhydrous and hydrated materials. In $Me_3SnNO_3{\cdot}H_2O$ (ref. 4) and $Me_3SnSO_3Ph{\cdot}H_2O$ (ref. 5) the water molecule is co-ordinated to the metal, and adjacent hydrated molecules are linked together by hydrogen bonds forming infinite linear chains. Nevertheless, the geometry at the tin in both anhydrous and hydrated materials is essentially the same.[5,6] In contrast, severe structural changes occur during the hydration of tin(II) chloride, which possesses the nine-co-ordinate $PbCl_2$-type structure when anhydrous.[7] Crystals of the dihydrate, $SnCl_2{\cdot}2H_2O$, consist of layers of pyramidal $SnCl_2{\cdot}H_2O$ units in which one water molecule is bonded directly to the tin. The second water molecule performs a different function, and connects adjacent layers by hydrogen bonds.[8] The water molecules in the complex salts $KCl{\cdot}KSnCl_3{\cdot}H_2O$ (refs. 9 and 10) and $KSnCl_3{\cdot}H_2O$ (ref. 11) are also isolated from the tin atoms, and again participate in complex systems of hydrogen-bonding.

Both the anhydrous (I) and monohydrated forms (II) of $Me_2Sn(ONH{\cdot}COMe)_2$ contain discrete molecular units in which each tin atom is six-co-ordinated by two methyl groups and two chelating *N*-acetylhydroxylamino-residues, although in surprisingly different fashions. The tin atoms in the anhydrous material (I) lie on crystallographic two-fold axes of symmetry lying on the bisector of the C–Sn–C angle, the two methyl groups occupying mutually *cis*-positions of a distorted octahedron (Figure 1). The two crystallographically independent molecules of the monohydrate (II), however, although having almost identical structures to each other, have geometries which are best described as distorted *trans*-octahedra (Figure 2). The stereochemistry at tin of $Me_2Sn(ONMe{\cdot}COMe)_2$ is therefore intermediate between the two, with a C–Sn–C 145.8(3)°,[2] compared with values of 109.1(4)° for (I) and 156.8(8)° (mean) for (II). The tin–carbon bond distances in the two materials are very similar [2.144(6) (I) and 2.15(2) Å (II)], but are longer than in $Me_2Sn(ONMe{\cdot}COMe)_2$.[2] As also observed for $Ph_3SnONPh{\cdot}COPh$ (ref. 12) and $Me_2Sn(ONMe{\cdot}COMe)_2$,[2] the chelation of the hydroxylamino-residues is unsymmetrical in both the anhydrous material and the hydrate, with each ligand forming one short, essentially covalent, and one long, essentially co-ordinate, tin–oxygen bond. The covalent tin–oxygen bond distance shows a monotonic decrease with decreasing C–Sn–C bond angle, but, whereas the co-ordinate tin–oxygen distances of the monohydrate and $Me_2Sn(ONMe{\cdot}COMe)_2$ (ref. 2) are similar, that in the anhydrous material is significantly shorter resulting in a much larger O–Sn–O bond angle subtended at tin by the chelating ligand (Table 6). The two molecules of the monohydrate contain an approximate mirror plane defined by the $Me_2Sn$ unit, but the two planar $\overline{Sn{\cdot}O{\cdot}N{\cdot}C{:}O}$ heterocyclic rings in each molecule are mutually twisted by 9.1°. The intra-ring bond

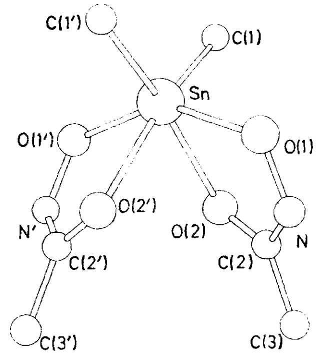

FIGURE 1 View of the stereochemistry about the tin atom in $Me_2Sn(ONH{\cdot}COMe)_2$, (I), illustrating the *cis*-octahedral configuration and the atom numbering system

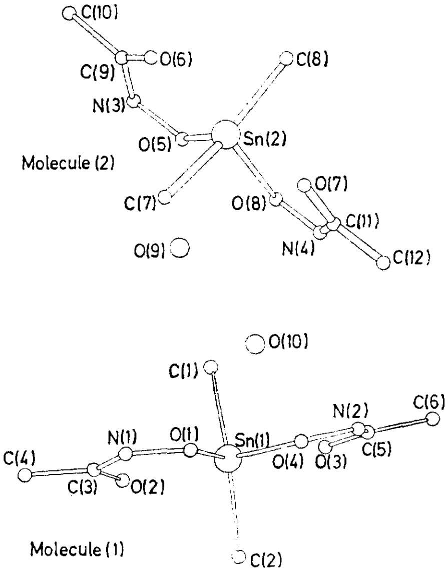

FIGURE 2 View of the relative orientation of the two crystallographically independent molecules in $Me_2Sn(ONH{\cdot}COMe)_2{\cdot}H_2O$, (II), showing atom numbering system

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[3] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1963.

[4] R. E. Drew and F. W. B. Einstein, *Acta Cryst.*, 1972, **B28**, 345.

[5] P. G. Harrison, R. C. Phillips, and J. A. Richards, *J. Organometallic Chem.*, 1976, **114**, 47.

[6] D. Potts, H. D. Sharma, A. J. Carty, and A. Walker, *Inorg. Chem.*, 1974, **13**, 1205.

[7] P. G. Harrison, *Co-ordination Chem. Rev.*, 1976, **20**, 1.

[8] H. Kiryama, K. Kitahama, G. Nakamura, and R. Kiryama, *Bull. Chem. Soc. Japan*, 1973, **46**, 1389.

[9] B. Kamenar and D. Grdenic, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1039.

[10] M. Falk, C.-H. Huang, and O. Knop, *Canad. J. Chem.*, 1974, **52**, 2380.

[11] M. Falk, C.-H. Huang, and O. Knop, *Canad. J. Chem.*, 1974, **52**, 2928.

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

distances of the heterocyclic rings are interesting. Those of $Me_2Sn(ONMe{\cdot}COMe)_2$ (ref. 2) and the monohydrate are quite similar, indicating a similar electronic distribution in the two compounds. Those in the anhydrous material, however, are all shortened at the expense of the carbonyl bond which is longer (Table 6). These changes, which are manifest of electronic redistribution, are most probably a result of different participations in hydrogen bonding by the oxygen and nitrogen atoms, rather than of the different geometries.

TABLE 6

Comparison of bond distances (Å) and angles (°) in (I) and (II) with those in related compounds

| Compound | C–Sn–C | Sn–C | Sn–O | Sn···O |
|---|---|---|---|---|
| (I) | 109.1(4) | 2.144(6) | 2.106(4) | 2.228(4) |
| (II) Molecule (1) | 156.7(7) | 2.15(1) | 2.16(2) | 2.35(1),<br>2.45(1) |
| Molecule (2) | 156.9(8) | 2.15(2) | 2.16(2) | 2.36(2),<br>2.43(2) |
| $Me_2Sn(ONMe{\cdot}COMe)_2$ [a] | 145.8(3) | 2.11(1) | 2.116(4) | 2.377(5) |
| $Ph_3SnONPh{\cdot}COPh$ [b] | | 2.14(1)<br>(eq.)<br>2.18(1)<br>(ax.) | 2.091(5) | 2.308(4) |

| Compound | O–Sn–O | N–O | C–N | C=O |
|---|---|---|---|---|
| (I) | 81.5(1) | 1.362(5) | 1.307(5) | 1.277(6) |
| (II) Molecule (1) | 71.4(4) | 1.40(2) | 1.32(3) | 1.25(3) |
| Molecule (2) | 71.6(5) | 1.37(3) | 1.34(3) | 1.25(4) |
| $Me_2Sn(ONMe{\cdot}COMe)_2$ | 71.3(1) | 1.38(1) | 1.31(1) | 1.25(1) |
| $Ph_3SnONPh{\cdot}COPh$ [b] | 71.3(2) | 1.38(1) | 1.30(1) | 1.26(1) |
| $HO{\cdot}NH{\cdot}COMe{\cdot}\frac{1}{2}H_2O$ [c] | | 1.40(1) | 1.33(1) | 1.245(6) |

[a] Ref. 2. [b] Ref. 12. [c] B. H. Bracher and R. W. H. Small, *Acta Cryst.*, 1970, **B26**, 1705.

Both lattices are strongly hydrogen-bonded. In (I) adjacent molecules are held together by two NH ··· O=C hydrogen bonds [N ··· O 2.82(2) Å] giving linear chains of molecules arranged perpendicular to the *b*-axis and parallel to the bisector of the β angle (Figure 3). The hydrogen-bonding system of (II) is, however, much more complex (Figure 4). Unlike the situation in (I), where hydrogen bonds involve oxygen atoms of the ligand carbonyl groups, these atoms in (II) do not participate in hydrogen-bond formation, but rather this involves the hydroxylamino-oxygen and nitrogen atoms [except for O(1) of molecule (1)] and the water molecules. Crystals of (II) are composed of alternate layers of $Me_2Sn(ONH{\cdot}COMe)_2$ and water molecules. Within each $Me_2Sn(ONH{\cdot}COMe)_2$ layer, the molecules are of the same crystallographic type, layers of each type alternating. Adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ molecules within each layer are connected *via* Sn–O ··· HN hydrogen bonds [molecule (1) O(4) ... N(1′) 2.92(2), molecule (2) O(8) ··· N(3′) 2.87(2) Å], whilst the water molecules serve to hold adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ layers together. Each water molecule is hydrogen-bonded to its two nearest-neighbour water molecules [O(10) ··· O(9) 2.73(3), O(10) ··· O(9′) 2.73(2) Å], and each forms two further hydrogen bonds with hydroxylamino-oxygen or nitrogen atoms of $Me_2Sn(ONH{\cdot}COMe)_2$ molecules in the nearest $Me_2Sn(ONH{\cdot}COMe)_2$ layer. One water molecule [O(9)] forms hydrogen bonds with one oxygen [O(5) $2.75_5$(2) Å] and one nitrogen atom [N(4″) 2.78(3) Å] from neighbouring type (2) $Me_2Sn(ONH{\cdot}COMe)_2$, the other [O(10)] forming hydrogen bonds with type (1) $Me_2Sn(ONH{\cdot}COMe)_2$ [O(4) 2.89(2), N(2″) 2.85(2) Å]. Each water molecule, therefore, participates in the formation of four hydrogen bonds, as does O(4) of each type (1) $Me_2Sn(ONH{\cdot}COMe)_2$ molecule. The participation in hydrogen bonding of the hydroxylamino-oxygen and nitrogen atoms of each of the four *N*-acetylhydroxylamino-residues is different (Table 7). The nitrogen and oxygen atoms of the two ligands of each type (2) $Me_2Sn(ONH{\cdot}COMe)_2$ molecule form one hydrogen bond to a

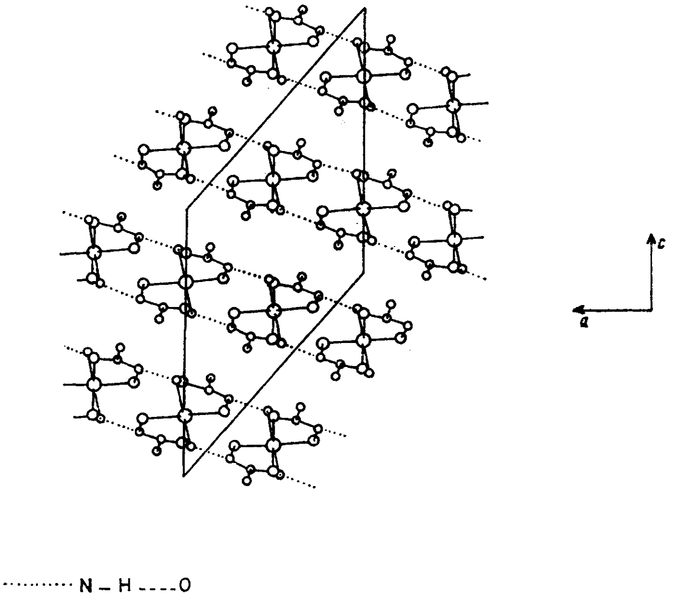

FIGURE 3 Projection of the unit cell of (I) on the *ac* plane; H bonds shown by dotted lines

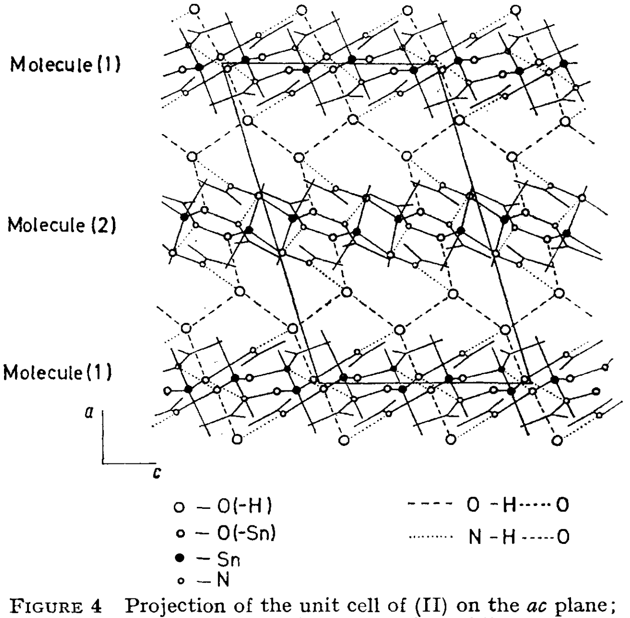

FIGURE 4 Projection of the unit cell of (II) on the *ac* plane; H bonds shown by dotted and dashed lines

water molecule and one intra-$Me_2Sn(ONH{\cdot}COMe)_2$-layer hydrogen bond, but the roles of the oxygen and nitrogen atoms are reversed in the two ligands. In one of the *N*-acetylhydroxylamino-ligands of type (1) $Me_2Sn(ONH{\cdot}COMe)_2$ molecules, the nitrogen atom [N(2)] forms a hydrogen bond with a water molecule whilst the oxygen atom of the same ligand [O(4)] forms hydrogen bonds with both a water molecule and also a nitrogen atom of an adjacent $Me_2Sn(ONH{\cdot}COMe)_2$. However, in the second ligand of each type (1) $Me_2Sn(ONH{\cdot}COMe)_2$ molecule, only the nitrogen atom [N(1)] participates in hydrogen bonding [with an oxygen atom of an adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ molecule in the same layer], whilst the oxygen atom of the ligand [O(1)] does not form any hydrogen bonds, the nearest possible contact being with the nitrogen atom of an adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ molecule in the same layer at 3.65 Å.

TABLE 7

Types of hydrogen bonds formed by the oxygen and nitrogen atoms of the *N*-acetylhydroxylamino-groups in the two crystallographically independent molecules of (II)

| Molecule (1) | | Molecule (2) | |
|---|---|---|---|
| Ligand (1) | Ligand (2) | Ligand (3) | Ligand (4) |
| N(1) : layer [a] | N(2) : water | N(3) : layer [a] | N(4) : water |
| O(1) : | O(4) : layer [b] and water | O(5) : water | O(8) : layer [b] |

[a] H bond to O of an adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ molecule in the same layer. [b] H bond to N of an adjacent $Me_2Sn(ONH{\cdot}COMe)_2$ molecule in the same layer.

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