# Crystal Structure of Anhydrous Nitrates and Their Complexes. Part VI.[1] Dimethyldinitratotin(IV)

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The title compound crystallises in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions: $a = 6{\cdot}36$, $b = 12{\cdot}07$, $c = 12{\cdot}18$ Å, $\beta = 121° 10'$. The structure was solved by the heavy-atom Patterson method and refined by a least-squares method in two independent investigations. The first of these gave $R$ 0·143 for 1074 reflections, and the second, $R$ 0·089 for 1258 reflections. The molecules occur in layers parallel to $(10\bar{1})$. Within each molecule the two nitrate groups are almost coplanar and are bonded to the tin atom in an unsymmetrical bidentate manner. The two C–Sn bonds (2·11 and 2·12 Å) make an angle of 144° and their plane is very nearly perpendicular to that of the nitrate groups.

TIN(IV) forms a series of anhydrous nitrates with the general formula $\mathrm{Me}_n\mathrm{Sn(NO_3)}_{4-n}$, $(n = 0 \cdots 3)$. Of these the structures of the tetra-[2] and the tri-nitrate[3] have previously been reported. The dinitrate structure was first determined by one of us in 1968[4] but because of unexpected differences in Sn–O bond lengths the whole structure has been independently redetermined. Both sets of results are reported in this paper.

## EXPERIMENTAL

The compound was prepared by the method reported by Addison *et al.*,[5] and single crystals were obtained by vacuum sublimation under static vacuum at 85 °C. It is extremely hygroscopic and crystals were therefore sealed in thin-walled glass capillaries under dry nitrogen. Crystals of dimensions *ca.* 0·5 × 0·3 mm were mounted about a needle axis. Oscillation, zero and first-layer Weissenberg photographs were obtained with Cu-$K_\alpha$ radiation and in the first determination these showed the crystal to be mounted about a monoclinic *b* axis, whilst in the second determination the crystal was mounted about a *c* axis for the space group $P2_1/n$. This *c* axis is the [101] diagonal axis in the *ac* face of the first $P2_1/c$ cell. The crystals were then transferred to a Hilger and Watts linear diffractometer for data collection and refinement of cell dimensions. In the first determination slow decomposition of the crystals was noted and higher layers were scaled appropriately by following the drop in intensity of standard reflections. In the second case rapid decomposition took place when about half of the data had been collected. A second crystal was therefore mounted to complete the data collection. The two sets of data in the second determination were scaled by comparing 25 zero-layer reflections between the two crystals. Refinement of the cell dimensions for the last crystal was also carried out on a Hilger and Watts four-circle diffractometer by use of a least-squares analysis of 12 reflections as described by Busing and Levy.[6] A total of 1121 independent reflections for the reciprocal lattice levels $h0$—$15l$ were recorded in the first case and 1395 reflections for the levels $hk0$—13 for the second case. Mo-$K_\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) was used with a scintillation counter and pulse-height discrimination.

The crystal data are as follows: $\mathrm{C_2H_6N_2O_6Sn}$, $M = 272{\cdot}78$, Monoclinic, $Z = 4$, $F(000) = 520$:

| | 1st Determn. | 2nd Determn. | |
|---|---|---|---|
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/c$ calc. from $P2_1/n$ |
| $a$ | 6·32 ± 0·02 | 6·36 ± 0·005 | 6·36 ± 0·005 |
| $b$ | 11·96 ± 0·04 | 12·07 ± 0·01 | 12·07 ± 0·01 |
| $c$ | 12·11 ± 0·04 | 10·43 ± 0·01 | 12·18 ± 0·015 |
| $\beta$ | 121° 18′ ± 10′ | 89° 41′ ± 4′ | 121° 10′ ± 4′ |
| $U$ | 783·7 Å$^3$ | 800·1 Å$^3$ | |
| $D_c$ | 2·31 g cm$^{-3}$ | 2·26 g cm$^{-3}$ | |
| $\mu$ | 32·5 cm$^{-1}$ | 32·0 cm$^{-1}$ | |

It may be fortuitous that all the cell dimensions in the second determination are larger than those in the first but the possibility of partial decomposition of the crystals affecting the cell dimensions cannot be ruled out.

The intensities were corrected for Lorentz and polarisation effects but no absorption corrections were made.

*Structure Determination.*—The position of the tin atom in each case was derived from a three-dimensional Patterson synthesis using $|F_o|^2$ as coefficients. A three-dimensional Fourier electron-density distribution was then computed using the signs for the structure factors derived from the tin position. A least-squares refinement of the tin position was carried out using unit weights. An $R$ value of 0·39 was obtained for tin only from the first set of data, and was reduced to 0·29 after five cycles of least-squares refinement. For the second set of data two cycles of refinement on tin only gave $R$ 0·38.

For the first determination the Fourier synthesis phased on the refined tin position revealed all the non-hydrogen atom positions in the asymmetric unit. Structure-factor calculations based on these positions gave $R$ 0·34. Two cycles of least-squares refinement on these positions with anisotropic thermal parameters and a weighting scheme such that $\sqrt{w} = 1$ if $|F_o| \leqslant F^*$ or $\sqrt{w} = F^*/|F_o|$ if $|F_o| > F^*$, where $F^*$ was set at 2000 and $F_o$ and $F^*$ are on a scale 50 × absolute, reduced $R$ to 0·17. At this stage 47 small high-angle reflections were excluded and $F^*$ was reduced to 1000. The refinement then converged after three further least-squares cycles to $R$ 0·143.

In the second determination a Fourier synthesis phased on the refined tin position revealed the positions of the nitrate groups. Further structure-factor and Fourier calculations enabled the carbon atom positions to be identified. Least-squares refinement of all the non-hydrogen atom positions, with isotropic thermal parameters, converged to $R$ 0·18. At this stage anisotropic thermal parameters were introduced and further least-squares refinement gave $R$ 0·12. The weighting scheme already described was then used with $F^*$ being given a value of 30.

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[1] Part V, C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1970, 3092.

[2] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1967, 1949.

[3] G. S. Brownlee, A. Walker, S. C. Nyburg, and J. T. Szymanski, *Chem. Comm.*, 1971, 1073.

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[5] C. C. Addison W. B. Simpson, and A. Walker, *J. Chem. Soc.*, 1964, 2360.

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

The lower value in this determination is due to the fact that $F_0$ and $F^*$ are on 10 times the absolute scale. In the last few cycles of refinement, reflections having $||F_o| - |F_c|| > 0{\cdot}5|F_o|$ were excluded from the least-squares calculations. In the last cycle there were 137 of these, mainly weak reflections. Excluding these, the final $R$ value was 0·089.

DISCUSSION

The two sets of final atomic and vibrational parameters are published with structure factor Tables for the second determination as Supplementary Publication No. 20558 (10 pp., 1 microfiche).* Bond lengths and angles are in Tables 1 and 2. The Figure shows the crystal structure seen in projection along the $a$ axis. All the tin atoms have $x$ co-ordinates close to zero so that the structure consists of layers of tin atoms parallel to (100) (Figure). However the molecules are tilted in such a way that they are better described as lying in layers parallel to (10$\bar{1}$), these layers being $a$/2 apart. The two nitrate groups in each molecule are very nearly coplanar (dihedral angle 1·7°) and their mean plane makes an angle with the (100) plane of 35·5°. The angle between the C–Sn–C plane and the mean plane of the two nitrate groups is 90·8°.

TABLE 1

Bond lengths (Å) with standard deviations in parentheses

| | 1st Determn. | 2nd Determn. |
|---|---|---|
| Sn–C(1) | 1·99(4) | 2·11(2) |
| Sn–C(2) | 2·01(5) | 2·12(2) |
| Sn–O(1) | 2·11(3) | 2·17(1) |
| Sn–O(3) | 2·38(2) | 2·42(1) |
| Sn–O(4) | 2·65(2) | 2·70(2) |
| Sn–O(6) | 2·12(2) | 2·15(1) |
| N(1)–O(1) | 1·29(3) | 1·31(2) |
| N(1)–O(2) | 1·33(4) | 1·22(2) |
| N(1)–O(3) | 1·18(4) | 1·26(2) |
| N(2)–O(4) | 1·20(4) | 1·23(2) |
| N(2)–O(5) | 1·28(4) | 1·21(2) |
| N(2)–O(6) | 1·34(3) | 1·35(2) |

TABLE 2

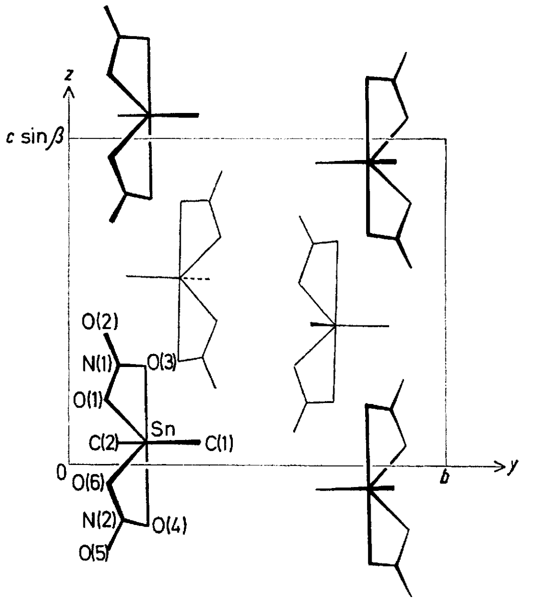
Bond angles (deg.) with standard deviations in parentheses

| | 1st Determn. | 2nd Determn. |
|---|---|---|
| C(1)–Sn–C(2) | 146(2) | 143·6(8) |
| C(1)–Sn–O(1) | 103(1) | 103·5(7) |
| C(1)–Sn–O(3) | 93(1) | 90·1(6) |
| C(1)–Sn–O(4) | 87(1) | 88·7(6) |
| C(1)–Sn–O(6) | 102(1) | 101·9(7) |
| C(2)–Sn–O(1) | 106(1) | 107·1(6) |
| C(2)–Sn–O(3) | 88(1) | 91·4(6) |
| C(2)–Sn–O(4) | 88(1) | 87·4(6) |
| C(2)–Sn–O(6) | 103(1) | 104·8(6) |
| O(1)–Sn–O(3) | 56(1) | 55·1(4) |
| O(1)–Sn–O(4) | 130(1) | 128·7(4) |
| O(1)–Sn–O(6) | 76(1) | 74·7(4) |
| O(3)–Sn–O(4) | 173(1) | 176·3(4) |
| O(3)–Sn–O(6) | 132(1) | 129·8(4) |
| O(4)–Sn–O(6) | 55(1) | 54·0(4) |
| O(1)–N(1)–O(2) | 126(3) | 123·2(13) |
| O(1)–N(1)–O(3) | 108(3) | 112·7(12) |
| O(2)–N(1)–O(3) | 125(3) | 124·1(13) |
| O(4)–N(2)–O(5) | 120(3) | 117·3(15) |
| O(4)–N(2)–O(6) | 123(3) | 122·2(13) |
| O(5)–N(2)–O(6) | 116(3) | 120·6(14) |
| Sn–O(1)–N(1) | 105(2) | 101·5(8) |
| Sn–O(3)–N(1) | 91(2) | 90·7(8) |
| Sn–O(4)–N(2) | 80(2) | 80·7(9) |
| Sn–O(6)–N(2) | 101(2) | 103·2(9) |

The closest contacts between molecules are:

| | | 1st Determn. | 2nd Determn. |
|---|---|---|---|
| N(1) · · · O(4) | $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ | 2·88 | 2·97 |
| N(2) · · · O(3) | $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ | 2·79 | 2·93 |
| O(1) · · · O(5) | $(1 - x, \bar{y}, \bar{z})$ | 3·09 | 3·11 |
| O(2) · · · O(4) | $(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ | 3·01 | 3·08 |
| O(3) · · · O(5) | $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ | 2·90 | 2·97 |

These are of the same order as the sum of the van der Waals radii for the atoms concerned.



The crystal structure seen in projection along the $a$ axis. Molecules shown with thick lines constitute the (10$\bar{1}$) layer of the $P2_1/c$ cell, passing through $x = 0$, $z = 0$, and $x = 1$, $z = 1$. Molecules with thin lines are in the parallel layer $a$/2 below this, passing through $x = 0$, $z = \frac{1}{2}$

Each nitrate group is co-ordinated to the tin atom in an unsymmetrical bidentate manner. Moreover the larger tin-oxygen bond is different in the two nitrate groups. In the first determination the larger values were 2·38 and 2·65 Å. It was because of this unexpected difference in the bond lengths that it was decided to undertake a second determination. The revised values of 2·42 and 2·70 Å would however imply that this difference is genuine. The shorter Sn–O distances are 2·12 and 2·11 Å in the first determination and 2·15 and 2·17 Å in the second. These compare with a mean Sn–O bond length of 2·16 Å in Sn(NO$_3$)$_4$ and of 2·128 Å for the shorter Sn–O bonds in MeSn(NO$_3$)$_3$. The longer Sn–O bonds in the latter compound have a mean of 2·290 Å so the bidentate bonding in this compound is not as unsymmetrical as in Me$_2$Sn(NO$_3$)$_2$. However, longer M–O bonds in unsymmetrically bidentate nitrate co-ordination have been found, *e.g.* 2·36, and 2·54 Å

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20. Structure factor Tables for the first determination are in ref. 4.

in $(Ph_4As)_2Co(NO_3)_4$ [7] and 2·653 Å in $Cu(NO_3)_2$-$(H_2O)_2,\frac{1}{2}H_2O$.[8] The increased Sn–O distances (and the increased Sn–C distances referred to later) found in the second determination are only partly accounted for by the larger cell dimensions. Variation in the severity of the diffraction effects of the tin atom due to differences in the data cut-off may account for the rest of the increase.

The arrangement of the co-ordinated groups around the central tin atom is best described in terms of two perpendicular planes, one being the C–Sn–C plane where the angle between the C–Sn–C is 143·6° (145·5° in the first determination). This corresponds to half of a distorted tetrahedral structure. The other plane contains the two nitrate groups in an arrangement very similar to that found in each of the two tin–nitrate planes in $Sn(NO_3)_4$. This therefore corresponds to half of a dodecahedral structure. This plane containing the tin atom and the nitrate groups nearly bisects the C(1)–Sn–C(2) angle, likewise the C–Sn–C plane very nearly bisects the 0(1)–Sn–O(6) angle. An alternative description of the structure would be in terms of a flattened tetrahedral arrangement in which each nitrate group is imagined to occupy one ligand position. The flattening of the tetrahedron is shown by the C–Sn–C angle of 143·6° (145·5° in the first determination) and the N–Sn–N angle of 130·5° (131·7° in the first determination).

In the nitrate groups it would be expected that the shortest N–O bond would be that not co-ordinated and the longest that to the oxygen more strongly co-ordinated to tin. This is found to be so for both nitrate groups in the second determination of $Me_2Sn(NO_3)_2$ and this is considered to be more accurate than the first determination in which some N–O distances seem anomalous. In general the structures of the nitrate groups are intermediate between those of uni- and bi-dentate nitrates with the group N(1), O(1)—(3) having a stronger resemblance to a bidentate group than the other grouping N(2),O(4)—(6) which appears more unindentate. Both structural studies give approximately equal Sn–C distances, although the values in the second determination are somewhat larger (by *ca.* 2σ). The mean values are 2·00 in the first and 2·12 Å in the second determination. This may be compared with 2·092 Å in $MeSn(NO_3)_3$.

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