The Crystal Structure of Trimethyltin Isocyanate-Hydroxide

By J. Benjamin Hall and Doyle Britton

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

Trimethyltin isocyanate-hydroxide, $(CH_3)_3SnNCO.(CH_3)_3SnOH$, forms monoclinic crystals in space group $P2_1/n$ with $a=11\cdot34(2)$, $b=13\cdot78(2)$, $c=8\cdot79(1)$ Å, and $\beta=99\cdot2(1)°$, with four molecules per unit cell. Using film techniques, 1088 independent observed reflections were collected. The resulting structure was refined by the least-squares method to an R value of $0\cdot136$. Chains of $(CH_3)_3Sn$ groups, bridged by alternating nitrogen atoms (from NCO) and oxygen atoms (from OH), are interconnected by NCO$\cdots$HO hydrogen bonds to form a layered structure. The Sn–N–Sn distances are $2\cdot43(5)$ and $2\cdot75(5)$ Å, and the Sn–O–Sn distances are $2\cdot15(5)$ and $2\cdot14(5)$ Å. The NCO$\cdots$(H)O hydrogen bonded distance is $2\cdot84(8)$ Å.

Introduction and experimental

As part of a study of intermolecular interactions in solids, the structure of trimethyltin isocyanate-hydroxide has been determined.* The crystals were originally thought to be trimethyltin cyanate.

A sample of $(CH_3)_3SnNCO$ (Thayer & Strommen, 1966) was provided several years earlier by R. West and J. S. Thayer. Sublimation of what was thought to be $(CH_3)_3SnNCO$ at a pressure between $0\cdot1$ and 1 mmHg with just enough heating to cause sublimation, yielded both hexagonal crystals of $(CH_3)_3SnNCO$ and monoclinic crystals found later to be $(CH_3)_3SnNCO.(CH_3)_3SnOH$.† An infrared spectrum taken after the structure of the monoclinic crystals was determined showed that the starting material was $(CH_3)_3SnNCO.(CH_3)_3SnOH$.

A new sample of the nonhydrolyzed compound $(CH_3)_3SnNCO$ was prepared according to the method reported by Thayer & Strommen (1966); only hexagonal crystals formed upon sublimation of this product. An infrared spectrum verified that the product was $(CH_3)_3SnNCO$. In an attempt to obtain enough monoclinic crystals for a chemical analysis, equimolar amounts of $(CH_3)_3SnNCO$ and $(CH_3)_3SnOH$ were

ground together and sublimed. This procedure yielded hexagonal $(CH_3)_3SnNCO$ crystals when sublimed at a lower temperature, and a mixture of crystals (none well enough formed to be classified by microscopic examination) at a higher temperature. Both the hexagonal $(CH_3)_3SnNCO$ crystals and the monoclinic $(CH_3)_3SnNCO.(CH_3)_3SnOH$ crystals melted at 105°, but $(CH_3)_3SnNCO$ appeared to change phase at 90°.

The cell dimensions, measured at room temperature from precession photographs (Mo Kα radiation, $\lambda = 0\cdot7107$ Å) are $a = 11\cdot34$ (2), $b = 13\cdot78$ (2), $c = 8\cdot79$ (1) Å, and $\beta = 99\cdot2$ (1)°. $P2_1/n$ is the only space group consistent with the systematic extinctions ($h0l$, $h+l = 2n+1$; $0k0$, $k=2n+1$). If $Z=4$, the molecular volume is 339 Å^3, compared to $180\cdot5$ Å^3 for $(CH_3)_3SnCN$ (Schlemper & Britton, 1966) and 155 Å^3 for

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* A preliminary study of trimethyltin azide-hydroxide, $(CH_3)_3SnN_3.(CH_3)_3SnOH$, (Thayer & West, 1964) was also made. The chemical history of this compound was very similar to that of the cyanate-hydroxide. An unambiguous sample of the azide-hydroxide melted at 140–142° compared to 120–121° reported for the azide. The unit-cell dimensions, $a=11\cdot25(2)$, $b=13\cdot74$ (2), $c=8\cdot69$ (1) Å, $\alpha=90\cdot0$ (1), $\beta=99\cdot1$ (1), $\gamma=90\cdot0$ (1)°, suggested that this compound is isomorphous with the cyanate-hydroxide, and the pattern of intensities is similar, but the symmetry of the $0kl$ precession photograph is only 2 rather than mm and the crystals are therefore triclinic. The structures clearly must be closely related, but they are not isomorphous. No further work is intended on the azide-hydroxide.

† The suggestion that the compound might be hydrolyzed was made by Professor R. West.

Table 1. *Final atomic parameters and standard deviations for trimethyltin isocyanate-hydroxide from full-matrix least-squares refinement*

	x	y	z	B
Sn(1)	0·2616 (3)	0·1247 (2)	0·2976 (4)	2·0 (1)*
Sn(2)	0·7600 (3)	0·3871 (3)	0·2532 (3)	2·3 (1)*
O(1)	0·208 (9)	0·355 (5)	−0·007 (9)	11·0 (21)
O(2)	0·773 (5)	0·436 (3)	0·025 (6)	5·9 (10)
N(1)	0·244 (4)	0·190 (3)	0·038 (5)	3·0 (9)
C(1)	0·240 (6)	0·267 (5)	0·032 (8)	4·5 (5)
C(11)	0·102 (6)	0·057 (4)	0·225 (9)	3·7 (12)
C(12)	0·282 (8)	0·271 (6)	0·385 (8)	5·6 (15)
C(13)	0·423 (7)	0·053 (5)	0·260 (8)	5·2 (15)
C(21)	0·593 (7)	0·314 (4)	0·189 (8)	4·7 (14)
C(22)	0·754 (7)	0·524 (5)	0·364 (9)	5·4 (16)
C(23)	0·920 (8)	0·298 (5)	0·293 (9)	6·0 (16)

Anisotropic thermal coefficients ($\times 10^4$)†

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn(1)	62 (5)	11 (2)	67 (6)	3 (2)	11 (3)	−7 (2)
Sn(2)	49 (6)	28 (2)	76 (5)	−12 (2)	8 (3)	−8 (2)

* Equivalent isotropic B.

† The anisotropic temperature factor has the form:
$\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$.

$(CH_3)_3SnOH$ (Kasai, Yasuda, & Okawara, 1965). The calculated density is 1·89 (1) g.cm^{-3}.

The compound formed sword-shaped crystals with (100) the prominent face; c is parallel to the sword direction. Weissenberg and precession intensity data (Mo $K\alpha$) were collected from crystals of dimensions 1·1 × 0·20 × 0·04 mm for the Weissenberg data and 3·0 × 0·25 × 0·04 mm for the precession data, with the c axis parallel to the spindle axis (c* for precession). Multiple-film Weissenberg data were collected for hk0–hk7, and precession data were collected for h0l and 0kl. The relative intensities were measured by

visual comparison with timed exposures of a single reflection. The data were intercorrelated by comparing all the reflections that occur on more than one film. In the region of reciprocal space explored there were 1088 independent observed reflections; this is approximately 40% of the independent reflections with sin $\theta/\lambda < 0·65$, the highest value observed. Lorentz, polarization, and spot-shape (Phillips, 1954) corrections were made. Absorption corrections were made using the actual crystal shape; the linear absorption coefficient, μ, for Mo $K\alpha$ radiation is 36·6 cm^{-1} (International Tables for X-ray Crystallography, 1959).

Table 2. *Observed and calculated structure factors* (× 1)

Determination and refinement of the structure

The structure was solved from three-dimensional Patterson and Fourier maps. The compound was first believed to be $(CH_3)_3SnNCO$ and consequently not all the cyanate atoms could be found. Professor West's suggestion that the compound might be hydrolyzed, plus packing considerations, led to the true identity of the compound and its structure. Full-matrix least-squares refinement was carried out on the positional and thermal parameters with the tin atoms treated as anisotropic.* Convergence was reached at an r value of 0·105 and an R value of 0·136, where $r = \sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^4$ and $R = \sum ||F_o| - |F_c||/\sum |F_o|$. The numerator of r was the function refined. The weights used were: $w = \frac{1}{2}$ for $F_o \le 16$, $w = 1$ for $16 < F_o \le 64$, and $w = (64/F_o)^4$ for $F_o > 64$. Refinements with and without anisotropic thermal parameters for the light atoms, made before the absorption corrections were

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* These calculations were made using programs *UMPREL*, *UMLSTSQ*, and *BADTEA*, written by Dr L. W. Finger, and *DATAP*2 (Coppens, Leiserowitz& Rabinovich, 1965). All the calculations were made on the Control Data 6600 computer of the University of Minnesota Computer Center.
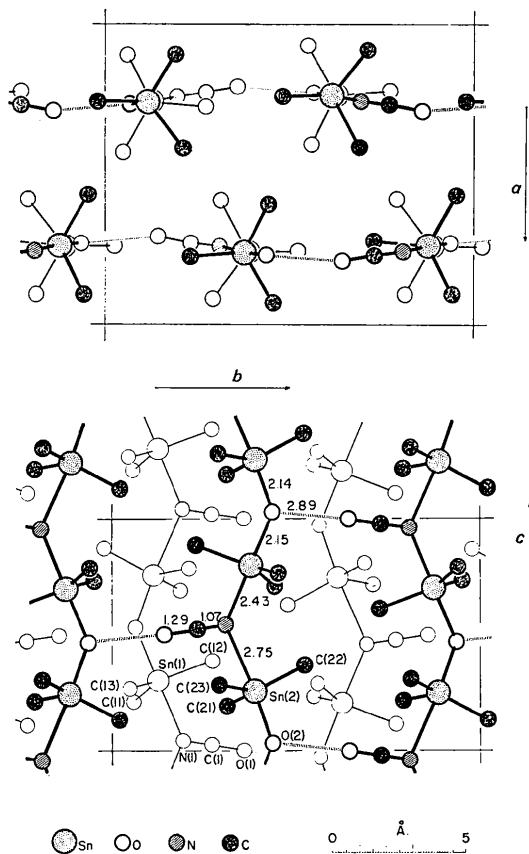

Fig. 1. The crystal structure of trimethytin isocyanate-hydroxide. The atoms drawn the heaviest are closer to the viewer, and the figure is one cell in depth starting at the face of the cell. Interatomic distances are given in Å.

made, indicated that refinement should be terminated with only the tin atoms anisotropic. The final parameters are given in Table 1. The observed and calculated structure factors are listed in Table 2.

Discussion

The crystal structure is shown in Fig. 1. Interatomic distances and angles are given in Fig. 1 and listed in Table 3. Chains of $(CH_3)_3Sn$ groups bridged by alternating nitrogen atoms (from NCO) and oxygen atoms (from OH) are interconnected by $NCO\cdots HO$ hydrogen bonds forming a layered structure. The infrared spectrum verifies the presence and degree of hydrogen bonding. The O–H peak is broadened and shifted to about 3450 cm^{-1}. Using 3700 cm^{-1} as a reference for a nonhydrogen bonded O–H stretching frequency, an oxygen-to-oxygen hydrogen bonded distance of 2·8 to 2·9 Å can be predicted (Lippincott & Schroeder, 1955). The distance determined from the crystal data is 2·89 (8) Å.

Table 3. *Bond lengths and angles for trimethyltin iso-cyanate-hydroxide*

(See also Fig. 1).

Sn(1)–C(11)	2·04 (7) Å
Sn(1)–C(12)	2·16 (8)
Sn(1)–C(13)	2·15 (8)
Sn(2)–C(21)	2·14 (7)
Sn(2)–C(22)	2·13 (7)
Sn(2)–C(23)	2·17 (8)
C(11)–Sn(1)–C(12)	125 (3)°
C(11)–Sn(1)–C(13)	118 (3)
C(12)–Sn(1)–C(13)	116 (3)
C(21)–Sn(2)–C(22)	116 (3)
C(21)–Sn(2)–C(23)	117 (3)
C(22)–Sn(2)–C(23)	121 (3)
O(2)–Sn(1)–C(11)	92 (3)
O(2)–Sn(1)–C(12)	93 (3)
O(2)–Sn(1)–C(13)	92 (2)
O(2)–Sn(2) C(21)	95 (3)
O(2)–Sn(2)–C(22)	99 (3)
O(2)–Sn(2)–C(23)	99 (3)
N(1)–Sn(1)–O(2)	178 (2)
N(1)–Sn(2)–O(2)	176 (2)
Sn(1)–N(1) –Sn(2)	135 (3)
Sn(1)–O(2) –Sn(2)	138 (3)
Sn(1)–N(1) –C(1)	121 (5)
N(1)—C(1)—O(1)	162 (9)
C(1)—O(1) –O(2)	158 (6)

The two Sn–O distances, 2·15(5) and 2·14(5) Å, are slightly longer than the normal Sn–O covalent distance of 2·05 Å (Sutton, 1965), but the compound might reasonably be thought of as $[(CH_3)_3Sn]_2OH^+$ ions alternating with NCO^- ions. The O–Sn–CH$_3$ angles are all slightly greater than 90° although they are far from tetrahedral. The two Sn–N distances, 2·43(5) and 2·75(5) Å, are between the normal Sn–N covalent radius of 2·1 Å and the estimated van der Waals

distance of 3·7 Å (Pauling, 1960).* The $(CH_3)_3Sn$ group that is closer to a nitrogen atom is also closer to planar, which is consistent, but it is not clear why the nitrogen bridge should be so unsymmetric.

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* The van der Waals radius of Sn was estimated by extrapolation of Pauling's values.

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Stereochemistry of Nucleic Acids and Their Constituents. XXI.* The Crystal and Molecular Structure of Bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) Perchlorate, a Degradation Product of Adenine N^1-Oxide

C. D. STOUT, M. SUNDARALINGAM† AND GEORGE HUNG-YIN LIN

Crystallography Laboratory, Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

The crystal and molecular structure of bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate, a degradation product of adenine N^1-oxide, has been determined by X-ray diffraction. 1458 three-dimensional intensity data were collected on a four-circle diffractometer, using Cu $K\alpha$ radiation. The structure was determined by the usual heavy-atom technique and refined by the method of full-matrix least-squares to a final R value of 0·052. The unit cell is monoclinic, space group $P2_1/c$ with $a = 4\cdot989 \pm 0\cdot001$, $b = 10\cdot883 \pm 0\cdot002$, $c = 16\cdot648 \pm 0\cdot002$ Å and $\beta = 90\cdot24 \pm 0\cdot01°$. The degradation product is formed by expulsion of C(2) of adenine and a rotation around the original C(5)–C(6) bond. This places N(1) in a *cis* planar configuration to N(7). Both N(1) and N(7) and their centrosymmetric partners form a square-planar complex around the copper. The coordination bond lengths are Cu–N(1) = 1·968 Å and Cu–N(7) = 1·970 Å. The N(1)–Cu–N(7) angle is 80·9°. The chelates are stacked in such a manner that the N(6) atoms of the centrosymmetrically related chelates above and below make the shortest contact, 3·136 Å, to the central copper atom. All potential hydrogen atoms are involved in the interionic hydrogen bonding scheme.

Introduction

As part of a program of research in these laboratories on the interaction of metal ions with nucleic acids and

their constituents we have undertaken a study of the crystal structure of bis-(4-aminoimidazole-5-carboxamidoxime)copper(II) perchlorate. Weiss & Venner (1969) who supplied this and several other similar complexes for our X-ray investigation believed that the complexes involved the ligand adenine N^1-oxide (Fig. 1). But the X-ray structure determination revealed that the ligand had undergone degradation to 4-aminoimidazole-5-carboxamidoxime with the expulsion of C(2). Apparently, the strong acidic condition and heat em-

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* Part XX of this series by J. Abola and M. Sundaralingam, *Acta Cryst.*, to be published. For related papers from these laboratories on metal binding studies, see Carrabine & Sundaralingam (1968, 1969, 1970, 1971), Sundaralingam & Carrabine (1969, 1971), and Sundaralingam, Stout & Hecht (1971).

† To whom correspondence should be addressed.