

Fig. 4. The ellipsoids of thermal motion with a probability of 50%.

and a MELCOM 9100 computer in our laboratory. Calculations of $|F_o|$, F_c , Fourier syntheses, diagonal least-squares, block-diagonal least-squares, bond lengths

and angles and best plane were carried out by *RDTR-3*, *RSSF-4*, *RSDL-3*, *HBL-IV*, *RSDA-4* and *RSBP-3* of the UNICS computer program system, respectively (*Crystallographic Society of Japan*, 1967). Thermal ellipsoids were plotted by the *ORTEP* program written by Johnson (1965).

The author thanks Professor Y. Saito and Dr F. Marumo for their encouraging interest and valuable discussion and Dr T. Haga for supplying crystals.

References

- AKISHIN, P. A., VILKOV, L. V. & TATEVSKII, V. M. (1958). *Dokl. Akad. Nauk SSSR*, **118**, 117.
- ALMENNINGEN, A., BASTIANSEN, O. & TRAETTEBERG, M. (1958). *Acta chem. Scand.* **12**, 1221.
- KARLE, I. L. & DRAGONETTE, K. S. (1965). *Acta Cryst.* **19**, 500.
- MACK, W. (1965). *Angew. Chem.* **77**, 260.
- MIURA, K. & HAGA, T. (1969). Presented at the 23rd Annual Meeting of the Chemical Society of Japan.
- SCHOMAKER, V. & PAULING, L. (1939). *J. Amer. Chem. Soc.* **61**, 1769.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.

Acta Cryst. (1972). **B28**, 345

The Crystal and Molecular Structure of Trimethyltin Nitrate Monohydrate

BY R. E. DREW AND F. W. B. EINSTEIN*

Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada

(Received 12 March 1971)

The crystal and molecular structure of the compound $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$ has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $C2/c$ with four formula units in a cell of dimensions $a=6.687(1)$, $b=11.495(1)$, $c=11.441(1)$ Å and $\beta=104.42(1)^\circ$. Refinement by full-matrix least-squares methods has given a conventional R value of 3.9% for the 463 observed reflexions. The tin atom has a slightly distorted trigonal bipyramidal environment consisting of a planar trimethyltin fragment with a unidentate nitrate group and a water molecule occupying the apical positions in a disordered manner. The Sn–O bonds are 2.22(3) Å (nitrate) and 2.47(2) Å (water). The mean Sn–CH₃ bond length is 2.11(2) Å. Intermolecular hydrogen bonding (O...O contact 2.72(3) Å) is proposed between the water of one molecule and the nitrate group of an adjacent molecule, leading to a one-dimensional polymeric linkage between molecules.

Introduction

Recently $\text{CH}_3\text{Sn}(\text{NO}_3)_3$, the remaining member of the series $(\text{CH}_3)_{4-n}\text{Sn}(\text{NO}_3)_n$ ($n=0, 1, 2, 3, 4$), was prepared and characterized by Ferraro, Potts & Walker (1970). The variation in the chemical and structural features of this series is of obvious interest. The second member of this group, anhydrous trimethyltin nitrate, has been

studied spectroscopically (Clark & O'Brien, 1963; Clark, O'Brien & Pickard, 1965; Yasuda & Okawara, 1965) along with its monohydrate, but the interpretations of their infrared spectra have been contradictory. Mössbauer studies of these two compounds (Cordery-Hayes, Peacock & Vuceli, 1967; Jones & Wood, 1970) have shown the very large quadrupole splittings of 4.14 (5) mm.sec⁻¹ for the anhydrous compound and 4.40 (5) mm.sec⁻¹ for the monohydrate. Thus, the tin nuclei in these compounds have asymmetric electric

* Author to whom correspondence should be addressed.

field gradients. Such asymmetry indicated structurally interesting features might be expected and prompted us to attempt the determination of the crystal structure of trimethyltin nitrate monohydrate.

Experimental

The preparation of anhydrous trimethyltin nitrate and its monohydrate has been described before by Yasuda & Okawara (1965) and by Clark & O'Brien (1963). The crystals used for this study were prepared by dissolving anhydrous trimethyltin nitrate in an acetone/dilute nitric acid mixture and allowing slow evaporation. A rectangular platelet was selected and cleaved to maximum dimensions $0.40 \times 0.30 \times 0.10$ mm in the directions **a**, **b**, and **c** respectively. This single crystal was mounted in a Lindemann glass capillary with the longest dimension parallel to the rotation axis, and yielded the complete diffraction data (obtained over a period of three weeks); during this time no significant decomposition was detected. However, after a period of a few months (or upon exposure to the atmosphere for a few days) these crystals took on a 'frosted' appearance.

Weissenberg photographs of the $0kl-2kl$ zones using Cu $K\alpha$ radiation, together with Mo $K\alpha$ precession photographs of the $h0l$ and $hk0$ zones, showed absences for hkl , $h+k=2n+1$; $h0l$, $l=2n+1$ ($h=2n+1$); $0k0$, ($k=2n+1$). This, combined with the Laue symmetry $2/m$, indicated either the space group Cc or $C2/c$.

Crystal data

Cell dimensions were determined by least-squares refinement of twenty high-angle reflexions whose 2θ values were accurately measured at 21°C on the diffractometer. A monoclinic cell, space group $C2/c$, of dimensions $a=6.687$ (1), $b=11.495$ (1), $c=11.441$ (1) Å and $\beta=104.42$ (1) $^\circ$ was obtained with $\lambda=0.70926$ Å for Mo $K\alpha_1$ radiation, $V=879.44$ (2) Å³, $Z=4$, $D_m=1.85$ (4) g.cm⁻³ in toluene (Berman density balance determination), $D_c=1.84$ g.cm⁻³, $F(000)=472$, and $\mu(\text{Mo } K\alpha)=28.8$ cm⁻¹ (the numbers in parentheses are the least-squares estimated standard errors).

In order to minimize multiple reflexions the crystal was deliberately misaligned so that it had a general orientation. Reflexion intensities for the unique set of data were measured on the manual Picker four-circle diffractometer, automated with the Picker FACS I system, using niobium-filtered Mo $K\alpha$ radiation, $\lambda=0.71069$ Å, and a scintillation detector with pulse-height analysis. Measurements for the inner set of data with $2\theta \leq 30^\circ$ were made at a scan rate of $2^\circ/\text{min}$ using a 1.2° take-off angle with a symmetrical $\theta-2\theta$ scan width of $1.6^\circ + 2 \tan \theta \cdot (\delta\lambda/\lambda)$ radians. The background intensity was determined by the normalization of two stationary background counts of 10 sec measured at both scan limits. An outer set of data for the range $30^\circ < 2\theta \leq 45^\circ$ was measured with the stationary-crystal

stationary-counter method using 20.0 sec peak counts and stationary background counts of 10 sec made symmetrically $0.8^\circ + \tan \theta \cdot (\delta\lambda/\lambda)$ radians in 2θ on either side of the reflexion peak. The two sets of data were initially combined using two scale factors determined by measurement of a number of reflexions by both techniques. Of the 556 intensities measured, 463 were above 1.8σ and were considered as observed reflexions ($\sigma = \sqrt{N}$ where N is the scan count plus the total normalized background count). Three standard reflexions were measured every two hours and retained a constancy within 1% over the entire data collection. Coincidence losses were checked by measurement of outstanding reflexions together with some intermediate intensities at lower incident beam strength; since a constant relationship was found, no coincidence losses were assumed. An experimental absorption curve in φ was determined at $\chi=90^\circ$; the intensity varied symmetrically about $\varphi=33^\circ$ with a periodicity of 90° and a maximum variation of 25% at $\varphi=123^\circ$. Approximate absorption corrections were applied to the intensity data according to this experimental curve and then Lorentz and polarization factors were applied to give structure factors in the usual manner.

Structure determination

A three-dimensional Patterson function* computed for the entire set of data revealed the tin atom for the asymmetric unit, which appeared to be on the special position $(0, y, \frac{1}{4})$. This was in agreement with the centrosymmetric space group $C2/c$. Two cycles of full-matrix least-squares refinement† of the two scale factors, the tin atom positional and isotropic temperature parameters (assuming an initial value of 2.0 Å²) were carried out yielding an unweighted conventional R_1 value‡ of 0.228. A three-dimensional electron-density map was computed from which the remaining non-hydrogen atoms were located. Least-squares refinement on these atomic positions and isotropic temperature factors brought the R_1 value down to 0.090. At this point an electron-density difference map revealed that the tin atom was moving anisotropically, and two cycles of least-squares refinement improved the agreement to 0.060. Further difference maps and least-squares refinement indicated that the x and z coordinates of the two coordinated oxygen atoms (which overlapped each other due to the twofold axis) should be interchanged, and also that the carbon atoms and water oxygen atom

* Program 'FORDAP, Crystallographic Fourier Summation with Optional Numeric and Alphanumeric Plotting and Peak Searching'. This program was obtained from the University of Canterbury (N.Z.) and originated from Dr A. Zalkin, University of California, Berkeley, U.S.A.

† Program 'BUCILS, Crystallographic Structure Factors and Full-Matrix Least-Squares'. This version is essentially the same as CUCILS 360/44 version from the University of Canterbury (N.Z.).

‡ R_1 is defined as $\sum(|F_o| - |F_c|) / \sum|F_o|$, and R_2 is defined as equal to $[\sum\omega(|F_o| - |F_c|)^2 / \sum\omega F_o^2]^{1/2}$.

were moving anisotropically. These additional changes lead to a final unweighted R_1 value of 0.039, and a weighted R_2 value[‡] of 0.052.

Our refinement of the structure leads to a disordered centrosymmetric model, the disorder involving the water and nitrate groups. Such a model is possible if one thinks of the crystal mosaic as a random assemblage of blocks of ordered unit cells, each block having one of the possible twofold related orientations. This results in the (pseudo-) crystallographic twofold axis which passes through the molecule. (Disorder at the molecular level is unlikely since chemically unacceptable intermolecular contacts result.) We considered that because the non-centrosymmetric model is chemically reasonable, it had to be extensively tested. The best agreement we obtained in a non-centrosymmetric model resulted in higher weighted and unweighted R values, the lowest unweighted R_1 value being 0.041. Furthermore, the high correlation coefficients between parameters involving the twofold related carbon atoms [C(1) and C(3)] and coordinated oxygen atoms, coupled with the increase in the number of variables, suggest that the structure was best described in the centrosymmetric model. A further confirmatory test for second harmonic generation (Harris, 1969) gave an inconclusive result (which is, however, consistent with the centrosymmetric model). It should be noted that there is no clear basis for rejecting an ordered non-centrosymmetric structure.

A weighting scheme where $\sigma = \sqrt{A}$ ($\omega = 1/\sigma^2$, $A = 7.7$) for all the data was used in the refinement down to an R_1 value of 0.05. The value of A was selected such that the error of fit,

$$[\sum \omega (|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2},$$

where (NO-NV) = the number of observations minus the number of variables, was 1.00. Refinement to convergence was carried out with $\sigma = \sqrt{A \cdot B/F}$ ($A = 2.1$, $B = 30.0$) for $F \leq 30.0$, $\sigma = \sqrt{A \cdot F/C}$ ($C = 18.0$) for $F > 30.0$, and $\sigma = \sqrt{D}$ ($D = 21.0$) for the unobserved reflexions (which appear with negative values of F_o in the

structure factor table) such that the error of fit was again equal to 1.00.

An electron-density difference map computed after the refinement was completed showed no positive peaks greater than $0.58 \text{ e.}\text{\AA}^{-3}$, although a negative through of $-0.82 \text{ e.}\text{\AA}^{-3}$ was found 0.92 \AA from the tin atom.

The scattering factors used throughout, including anomalous scattering for the tin atom, were taken from the *International Tables of X-ray Crystallography* (1968) (Atom multipliers of $\frac{1}{2}$ were applied to both of the atoms on special positions and the disordered atoms).

Table 1. *Final positional* ($\times 10^3$) *and thermal parameters for* $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$

Estimated standard deviations of the least significant figures are given in parentheses here and in subsequent tables.

	x/a	y/b	z/c	$B (\text{\AA}^2)$
Sn	0	99.7 (1)	250.0	*
C(1)	36 (2)	196 (2)	98 (1)	*
C(2)	0	-84 (2)	250	*
N	456 (3)	38 (2)	402 (2)	6.6 (8)
O(1)	335 (4)	116 (2)	336 (2)	6.4 (13)
O(2)	645 (3)	14 (2)	424 (2)	9.4 (9)
O(3)	364 (3)	11 (2)	474 (2)	8.3 (8)
O(4)	-381 (3)	90 (2)	195 (2)	*

* Anisotropic thermal parameters were used for these atoms. The form of the anisotropic thermal ellipsoid is $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

The values of β_{ij} are multiplied by 10^3 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	30.5 (5)	10.3 (2)	9.4 (2)	0.0	-4.0 (1)	0.0
C(1)	48 (4)	20 (2)	13 (1)	-6 (2)	-7 (2)	8 (1)
C(2)	67 (8)	8 (1)	17 (2)	0.0	-4 (3)	0.0
O(4)	14 (3)	18 (2)	8 (2)	-2 (2)	-7 (2)	-5 (2)

The final positional and thermal parameters, interatomic distances and angles, and mean planes are shown in Tables 1, 3 and 5 respectively. The observed and final lists of calculated structure factors are shown in Table 2, while Table 4 gives the root-mean-square amplitudes of vibration along axes of the thermal

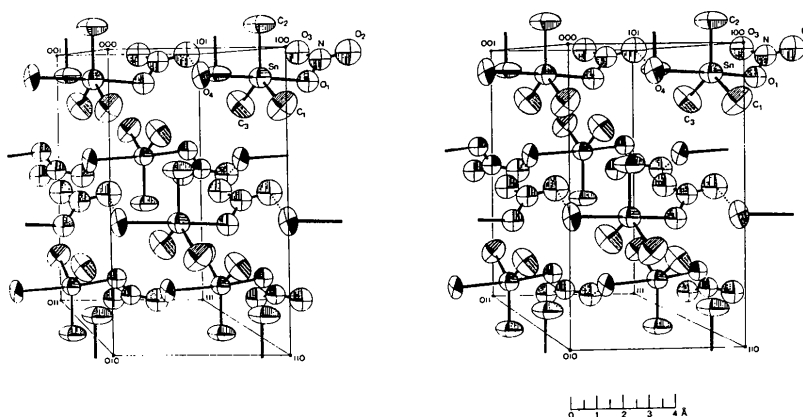


Fig. 1. Stereoscopic crystal packing diagram for $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$, with 50% probability thermal ellipsoids.

Table 2. Measured and calculated structure factors for $(CH_3)_3SnNO_3 \cdot H_2O$

The unobserved reflexions which were not significantly above background have been indicated by a negative F_{obs} .

K	L	Obs	Calc	**** h = 1 ****				**** h = 5 ****				**** h = 7 ****																										
0	0	0	0	1	0	98	89	0	8	67	69	3	7	38	39	0	4	50	-49	7	9	17	15	1	6	22	-19											
0	0	0	0	1	1	90	-84	2	10	35	-35	3	8	17	-16	5	3	-6	4	6	5	31	31	9	2	18	18	1	7	15	19							
0	0	0	0	1	2	141	-130	2	2	49	-49	5	1	-7	-P	1	0	61	51	8	9	37	10	6	6	19	18	9	2	20	-25	1	8	19	21			
0	0	0	0	1	3	13	41	2	3	124	121	5	2	89	86	1	1	40	-40	5	6	73	72	6	7	20	-19	9	3	17	-10	1	9	-7	-8			
0	0	0	0	1	4	95	-93	2	4	50	-51	5	3	-6	-1	1	4	34	30	5	4	37	-2	6	10	20	20	9	6	17	-15	3	4	-6	6			
0	0	0	0	1	5	56	-55	2	5	103	-103	5	4	76	-76	1	5	26	-27	5	10	26	27	8	1	44	47	7	7	-8	-11	3	3	37	37			
0	0	0	0	1	6	77	-78	2	6	36	-33	5	7	6	-6	1	6	34	-34	5	11	-2	1	8	2	13	-15	11	1	-15	-15	3	4	-7	-15			
0	0	0	0	1	7	62	-60	2	7	16	-17	5	6	46	-46	0	6	40	-40	5	12	16	-14	7	3	17	-17	11	3	-19	1	6	-7	12	-12			
0	0	0	0	1	8	71	-68	2	8	15	-17	5	7	-6	-1	1	4	47	-47	7	2	41	42	8	4	-7	1	11	3	-19	1	6	-7	12	-12			
0	0	0	0	1	9	77	-78	2	9	38	-43	5	8	32	-32	2	8	28	-28	7	1	60	-66	8	5	31	30	9	2	13	-13	3	7	-2	21	-21		
0	0	0	0	1	10	82	-80	2	10	17	-19	7	0	17	-17	3	9	24	-24	7	3	54	-56	7	6	21	19	9	6	-6	-7	8	-7	8	-7			
0	0	0	0	1	11	86	-84	2	11	29	-29	4	9	55	-55	3	4	47	-47	7	4	57	55	8	7	36	34	10	3	-13	-13	3	9	15	-16	-16		
0	0	0	0	1	12	91	-88	2	12	41	-41	4	1	54	-57	7	2	24	-24	9	3	65	-65	7	6	21	19	8	7	-7	17	17	5	1	-7	10	-7	
0	0	0	0	1	13	93	-91	2	13	54	-54	4	2	53	-55	7	6	17	-17	9	5	74	-74	8	8	14	14	9	8	-8	-9	10	10	5	1	-7	10	-7
0	0	0	0	1	14	95	-93	2	14	67	-67	4	3	51	-55	7	5	31	-35	9	4	87	-87	10	10	16	16	10	11	-10	-10	6	6	5	-7	5	-7	
0	0	0	0	1	15	96	-94	2	15	80	-80	4	4	51	-57	7	4	17	-13	11	1	100	-100	11	11	17	-16	14	1	-7	-10	6	6	5	-7	5	-7	
0	0	0	0	1	16	97	-95	2	16	93	-93	4	5	51	-57	7	5	31	-35	12	2	113	-113	12	12	18	-17	15	2	13	-13	7	7	6	-7	6	-7	
0	0	0	0	1	17	98	-96	2	17	106	-104	4	6	48	-56	7	6	17	-17	13	3	124	-124	13	13	19	-18	16	3	15	-15	8	8	7	-8	7	-8	
0	0	0	0	1	18	99	-97	2	18	119	-117	4	7	47	-55	7	7	17	-17	14	4	136	-136	14	14	20	-19	17	4	17	-17	9	9	8	-9	8	-9	
0	0	0	0	1	19	100	-98	2	19	132	-130	4	8	46	-54	7	8	17	-17	15	5	148	-148	15	15	21	-20	18	5	19	-19	10	10	9	-10	9	-10	
0	0	0	0	1	20	101	-99	2	20	145	-143	4	9	45	-53	7	9	17	-17	16	6	160	-160	16	16	22	-21	19	6	20	-20	11	11	10	-11	10	-11	
0	0	0	0	1	21	102	-100	2	21	158	-156	4	10	44	-52	7	10	17	-17	17	7	172	-172	17	17	23	-22	20	7	21	-21	12	12	11	-12	11	-12	
0	0	0	0	1	22	103	-101	2	22	171	-169	4	11	43	-51	7	11	17	-17	18	8	184	-184	18	18	24	-23	21	8	22	-22	13	13	12	-13	12	-13	
0	0	0	0	1	23	104	-102	2	23	184	-182	4	12	42	-50	7	12	17	-17	19	9	196	-196	19	19	25	-24	22	9	23	-23	14	14	13	-14	13	-14	
0	0	0	0	1	24	105	-103	2	24	197	-195	4	13	41	-49	7	13	17	-17	20	10	208	-208	20	20	26	-25	23	10	24	-24	15	15	14	-15	14	-15	
0	0	0	0	1	25	106	-104	2	25	210	-208	4	14	40	-48	7	14	17	-17	21	11	220	-220	21	21	27	-26	24	11	25	-25	16	16	15	-16	15	-16	
0	0	0	0	1	26	107	-105	2	26	223	-221	4	15	39	-47	7	15	17	-17	22	12	230	-230	22	22	28	-27	25	12	26	-26	17	17	16	-17	16	-17	
0	0	0	0	1	27	108	-106	2	27	236	-234	4	16	38	-46	7	16	17	-17	23	13	240	-240	23	23	29	-28	26	13	27	-27	18	18	17	-18	17	-18	
0	0	0	0	1	28	109	-107	2	28	249	-247	4	17	37	-45	7	17	17	-17	24	14	250	-250	24	24	30	-29	27	14	28	-28	19	19	18	-19	18	-19	
0	0	0	0	1	29	110	-108	2	29	262	-260	4	18	36	-44	7	18	17	-17	25	15	260	-260	25	25	31	-30	28	15	29	-29	20	20	19	-20	19	-20	
0	0	0	0	1	30	111	-109	2	30	275	-273	4	19	35	-43	7	19	17	-17	26	16	270	-270	26	26	32	-31	29	16	30	-30	21	21	20	-21	20	-21	
0	0	0	0	1	31	112	-110	2	31	288	-286	4	20	34	-42	7	20	17	-17	27	17	280	-280	27	27	33	-32	30	17	31	-31	22	22	21	-22	21	-22	
0	0	0	0	1	32	113	-111	2	32	301	-299	4	21	33	-41	7	21	17	-17	28	18	290	-290	28	28	34	-33	31	18	32	-32	23	23	22	-23	22	-23	
0	0	0	0	1	33	114	-112	2	33	314	-312	4	22	32	-40	7	22	17	-17	29	19	300	-300	29	29	35	-34	32	19	33	-33	24	24	23	-24	23	-24	
0	0	0	0	1	34	115	-113	2	34	327	-325	4	23	31	-39	7	23	17	-17	30	20	310	-310	30	30	36	-35	33	20	34	-34	25	25	24	-25	24	-25	
0	0	0	0	1	35	116	-114	2	35	340	-338	4	24	30	-38	7	24	17	-17	31	21	320	-320	31	31	37	-36	34	21	35	-35	26	26	25	-26	25	-26	
0	0	0	0	1	36	117	-115	2	36	353	-351	4	25	29	-37	7	25	17	-17	32	22	330	-330	32	32	38	-37	35	22	36	-36	27	27	26	-27	26	-27	
0	0	0	0	1	37	118	-116	2	37	366	-364	4	26	28	-36	7	26	17	-17	33	23	340	-340	33	33	39	-38	36	23	37	-37	28	28	27	-28	27	-28	
0	0	0	0	1	38	119	-117	2	38	379	-377	4	27	27	-35	7	27	17	-17	34	24	350	-350	34	34	40	-39	37	24	38	-38	29	29	28	-29	28	-29	
0	0	0	0	1	39	120	-118	2	39	392	-390	4	28	26	-34	7	28	17	-17	35	25	360	-360	35	35	41	-40	38	25	39	-39	30	30	29	-30	29	-30	
0	0	0	0	1	40	121	-119	2	40	405	-403	4	29	25	-33	7	29	17	-17	36	26	370	-370	36	36	42	-41	39	26	40	-40	31	31	30	-31	3		

Sn-ONO₂ bond in (CH₃)₃SnNO₃·H₂O to be somewhat shorter than is found. However, this bond is not as long as the Sn-O distance of 2.251 (16) Å in (CH₃)₂(C₅H₅NO)₂SnCl₂ (Bloom, Penfold & Robinson, 1969), or the long Sn-OH₂ distance of 2.47 (2) Å in the same molecule.

Table 3. *Interatomic distances (Å) and angles (°) with their estimated standard deviations*

(a) Intramolecular bonded contacts

Sn-C(1)	2.12 (1) [2.16 (1)]*	N-O(1)	1.33 (3)
Sn-C(2)	2.10 (2) [2.14 (2)]*	N-O(2)	1.26 (2)
Sn-O(1)	2.22 (3)	N-O(3)	1.18 (2)
Sn-O(4)	2.47 (2)		

* These values are the interatomic distances averaged over thermal motion with the second atom assumed to ride on the first. This correction was applied according to the model used by W. R. Busing, K. O. Martin & H. A. Levy in their program, 'ORFEE, A Fortran Crystallographic Function and Error Program'. (S.F.U. version, 1970).

(b) Intramolecular non-bonded contacts shorter than 3.0 Å

O(1)-O(2)	2.38 (3)
O(1)-O(3)	1.98 (3)
O(2)-O(3)	2.10 (3)

(c) Intermolecular contacts shorter than 3.0 Å

O(4)-O(1)†	2.77 (3)
O(4)-O(2)†	2.72 (3) (Hydrogen Bond)
O(4)-N†	2.91 (3)
O(4)-O(3)‡	2.92 (3)

(d) Intramolecular bond angles

C(1)-Sn-C(2)	121.3 (5)	Sn-O(1)-N	127 (2)
C(1)-Sn-O(1)	90.1 (8)	O(1)-N-O(2)	134 (2)
C(1)-Sn-O(4)	97.7 (7)	O(1)-N-O(3)	104 (2)
C(2)-Sn-O(1)	94.8 (6)	O(2)-N-O(3)	118 (2)
C(2)-Sn-O(4)	87.4 (5)		
O(1)-Sn-O(4)	169.3 (8)		

(e) Intermolecular contact angles

Sn-O(4)-O(1)†	131.3 (6)	‡O(3)-O(4)-O(1)†	101.7 (7)
Sn-O(4)-O(2)†	87.5 (7)	‡O(3)-O(4)-O(2)†	126 (1)
Sn-O(4)-N†	112.1 (8)	‡O(3)-O(4)-N†	111.7 (9)
Sn-O(4)-O(3)‡	125.6 (9)		

†‡ This refers to the atom following the symmetry transformation:

$$\begin{aligned} \dagger & (1-x, y, z) \\ \ddagger & (1-x, -y, \frac{1}{2}+z) \end{aligned}$$

Table 4. *Root-mean-square amplitudes of vibration (Å) along axes of the thermal ellipsoids*

	Principal axis	Axis 1	Axis 2
Sn	0.194 (3)	0.263 (2)	0.319 (2)
C(1)	0.21 (2)	0.31 (2)	0.45 (2)
C(2)	0.22 (2)	0.29 (2)	0.43 (2)
O(4)	0.06 (4)	0.28 (2)	0.37 (3)

Examination of the anisotropic thermal parameters of the trimethyltin fragment is consistent with the description of the group as a rigid body. The oscillation is about an axis, passing through the tin atom and normal to the plane of the group, while the principle tin atom thermal motion is out of the plane of the group

Table 5. *Mean planes† as Ax + By + Cz + D = 0*

The normal equation of a plane, expressed in Å, refers to the orthogonalized set of axes *x, y, z* (corresponding to *a, b, and c**), the direction cosines of the normal to the plane, *A, B, and C*, and the distance of the plane from the origin, *D*.

(a) Plane of the trimethyltin fragment

$$(-0.9292)x + (0.0000)y + (-0.3696)z - (-0.3620) = 0$$

(b) Plane of the nitrate group (weighted)

$$(-0.1588)x + (-0.7691)y + (-0.6190)z - (-3.4886) = 0$$

$\chi^2 = 6.81$	Deviation from plane (Å)
N	0.09 (4)
O(1)	-0.03 (5)
O(2)	-0.04 (4)
O(3)	-0.03 (4)

Angle between the two planes is 68°.

† Calculated by 'Program Meanplane, Calculation of Weighted Mean Planes through Atom Groups with e.s.d.'s', S.F.U. 360 version of the program written by M. E. Pippy & F. R. Ahmed at the National Research Council of Canada.

The dihedral angle between the plane of the nitrate group and the plane of the trimethyltin fragment is 68° (see Table 5), whereas the Sn-O(1)-N angle is 127 (2)°. The N-O(1) bond length of 1.33 (3) Å is comparable to those of 1.34 (4) Å in [Au(NO₃)₄]⁻ (Garner & Wallwork, 1969) and 1.32 (1) Å in Pd(NO₃)₂·2(CH₃)₂SO (Langs, Hare & Little, 1967), but shorter than the 1.40 (1) Å in C(CH₂ONO₂)₄ (Trotter, 1963), 1.45 (3) Å in VO(NO₃)₃·CH₃CN (Einstein, Enwall, Morris & Sutton, 1971), and 1.41 (1) Å in *cis*-1,2-acenaphthenediol dinitrate (Mak & Trotter, 1964). Of possible significance is the difference between the N-O(2) bond length of 1.26 (2) Å and the N-O(3) bond length of 1.18 (2) Å. Similar inequalities have been observed in other unidentate nitrate groups, for which there were various explanations (Einstein, Enwall, Morris & Sutton, 1971; Garner & Wallwork, 1969). The difference in this structure can be accounted for in terms of hydrogen bonding. The longer N-O(2) bond is associated with an intermolecular O(2) to O(4) (water) contact distance of 2.72 (3) Å, which would reduce the amount of double bond character in the N-O(2) bond. Hydrogen bonding does not account for the unusual angles in this nitrate group.

The hydrogen bonding proposed leads to a one-dimensional polymeric linkage between molecules. In addition, an intermolecular contact distance of 2.77 (3) Å is observed between oxygen atoms O(4) and O(1). This could be interpreted as a three-centered hydrogen bond between oxygen atoms O(4), O(2) and O(1), but this seems unlikely since the oxygen atom O(1) is coordinated to the tin atom. It is also interesting to note that a third intermolecular contact of 2.92 (3) Å exists between the water oxygen atom [O(4)] and the nitrate oxygen atom [O(3)] of a third molecule, with an O(2)···O(4)···O(3) angle of 126 (1)°, an O(1)···O(4)···O(3) angle of 101.7 (7)°, and a mean angle of

114°. Although this latter contact distance represents a rather weak hydrogen bond, it is geometrically feasible.

Since previous interpretations (Yasuda & Okawara, 1965; Clark, O'Brien & Pickard, 1965) of the infrared spectrum of $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$ are not consistent with the structure determined in this study, we suggest that the assignment of the 510 cm^{-1} band to the Sn-C symmetric stretching mode is incorrect, and that it is more likely to be a Sn-O stretch. In the infrared spectrum of anhydrous $(\text{CH}_3)_3\text{SnNO}_3$ (Clark & O'Brien, 1963; Clark, O'Brien & Pickard, 1965), Clark *et al.* (1965) made a similar suggestion for their previous assignment (1963) of the 520 cm^{-1} band. The shifts to lower frequencies, from 557 to 540 cm^{-1} (asymmetric Sn-C stretch), and from 520 to 510 cm^{-1} (Sn-O stretch), in going from anhydrous $(\text{CH}_3)_3\text{SnNO}_3$ to $(\text{CH}_3)_3\text{SnNO}_3 \cdot \text{H}_2\text{O}$, indicate differences in the bonding. An examination of the crystal structure of anhydrous $(\text{CH}_3)_3\text{SnNO}_3$ is in progress.

We wish to thank the National Research Council of Canada whose financial support made this work possible.

References

- BLOOM, E. A., PENFOLD, B. R. & ROBINSON, W. T. (1969). *J. Chem. Soc. (A)*, p. 913.
- CLARK, H. C. & O'BRIEN, R. J. (1963). *Inorg. Chem.* **2**, 740.
- CLARK, H. C., O'BRIEN, R. J. & PICKARD, A. L. (1965). *J. Organomet. Chem.* **4**, 43.
- CLARK, H. C., O'BRIEN, R. J. & TROTTER, J. (1964). *J. Chem. Soc.* p. 2332.
- CORDEY-HAYES, M., PEACOCK, R. D. & VUCELI, M. (1967). *J. Inorg. Nucl. Chem.* **29**, 117.
- EINSTEIN, F. W. B., ENWALL, E., MORRIS, D. M. & SUTTON, D. (1971). *Inorg. Chem.* **10**, 678.
- EINSTEIN, F. W. B. & PENFOLD, B. R. (1968). *J. Chem. Soc. (A)*, p. 3019.
- FERRARO, J. R., POTTS, D. & WALKER, A. (1970). *Canad. J. Chem.* **48**, 711.
- GARNER, C. D., SUTTON, D. & WALLWORK, S. C. (1967). *J. Chem. Soc. (A)*, p. 1949.
- GARNER, C. D. & WALLWORK, S. C. (1969). *Chem. Commun.* p. 108.
- GORSICH, R. D. (1962). *J. Amer. Chem. Soc.* **84**, 2486.
- HARRIS, S. C. (1969). *Chromatrix Technical Letters*, Number 1, May.
- International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.
- JONES, C. & WOOD, E. (1970). Private communication.
- LANGS, D. A., HARE, C. R. & LITTLE, R. G. (1967). *Chem. Commun.* p. 1080.
- MAK, T. C. W. & TROTTER, J. (1964). *Acta Cryst.* **17**, 367.
- MUETTERTIES, E. L. & SCHUNN, R. A. (1966). *Quart. Rev.* p. 245.
- PARISH, R. V. & PLATT, R. H. (1969). *J. Chem. Soc. (A)*, p. 2146.
- PARISH, R. V. & PLATT, R. H. (1970). *Inorg. Chim. Acta*, **4**, 1.
- SCHLEMPER, E. O. (1967). *Inorg. Chem.* **11**, 2012.
- SCHLEMPER, E. O. & HAMILTON, W. C. (1966). *Inorg. Chem.* **5**, 995.
- TROTTER, J. (1963). *Acta Cryst.* **16**, 698.
- YASUDA, K. & OKAWARA, R. (1965). *J. Organomet. Chem.* **3**, 76.

Acta Cryst. (1972). B28, 350

The Crystal Structure of 1,8-Naphthyridine

BY A. CLEARFIELD, M. J. SIMS AND P. SINGH

Department of Chemistry, Ohio University, Athens, Ohio 45701, U.S.A.

(Received 19 March 1971)

The crystal structure of 1,8-naphthyridine, $\text{C}_8\text{H}_6\text{N}_2$, has been determined by a symbolic-addition procedure and was refined to an R of 4.8% by block-diagonal least-squares methods. The unit cell is monoclinic, $P2_1/c$, with $a = 6.170(8)$, $b = 10.485(6)$, $c = 11.454(8)$ Å, $\beta = 117.66(8)^\circ$, and 4 molecules per unit cell. Intensity data were collected on a Picker manually driven 4-circle goniometer using the θ - 2θ scan method. The molecule is nonplanar with the two rings twisting in opposite directions about the bridgehead carbon-carbon bond. This results from the repulsion of the lone-pair electrons on the nitrogen atoms, since other naphthyridines are planar as is the 1,8-naphthyridine when it is chelated to a metal atom.

Introduction

Recently, 1,8-naphthyridine complexes of transition metal cations have been prepared (Bodner & Hendrickson, 1970). The crystal structure of the tetrakis(1,8-naphthyridine)iron(II) perchlorate complex was sub-

sequently determined and shown to contain a unique eight-coordinate iron(II) ion (Hendrickson & Bodner, 1970; Clearfield, Singh & Bernal, 1970; Singh, Clearfield & Bernal, 1971). In this complex the ligands are bonded to the iron atom through the nitrogen lone pairs. The N(1)-C(8a)-N(8) outer bridgehead bond