The Crystal Structure of Potassium Triformatostannate (II), KSn(HCOO)$_3$

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The crystal structure of KSn(HCOO)$_3$ has been determined. The material crystallises in the monoclinic system with $a = 6.123_4$, $b = 17.64_8$, $c = 6.965_5$ Å, $\beta = 92.13_6°$, and space group $P2_1/c$. There are four formula units in the unit cell.

The positions of tin, potassium, oxygen, and carbon atoms were found from three-dimensional Patterson and Fourier functions. Full matrix least-squares refinement of the structure, based on 1087 independent reflexions, gave a final R value of 0.075.

The structure is built up from close-packed potassium and triformatostannate(II) ions. The tin atom in the anion is bonded covalently to three formate groups which have a unidentate function, the Sn—O bond distances being 2.13$_9$, 2.17$_4$ and 2.18$_2$ Å. The three oxygen atoms are on one side of the tin atom, giving a pyramidal configuration.

The structure of KSn(HCOO)$_3$ is discussed with reference to previous physico-chemical studies on this material and to the known structures of some other tin(II) compounds.

The present work has been undertaken as part of a study of the structures and bonding of tin(II) compounds.[16] As there is only some indirect information on the nature of tin(II) carboxylates, it was thought profitable to investigate the structure of potassium triformatostannate(II). The preparation and properties of this compound have been studied by Donaldson and Knifton,[1] who report that it is the most stable member of a series of triformatostannates(II) (MSn(HCOO)$_3$ where M = K, Rb, Cs, and NH$_4$) which are probably isostructural.

EXPERIMENTAL

Crystals of potassium triformatostannate(II) were prepared according to the published method.[1] Colourless rectangular plates, elongated along the a axis, or stout prisms were obtained. The crystal selected for investigation was a plate of length 0.25 mm (a axis direction) and cross-section 0.113 mm (c axis) × 0.022 mm (b axis). With the a axis as rotation axis, equi-inclination Weissenberg photographs corresponding to the layers

$0kl-5kl$ were recorded by the multiple film technique, six films being obtained for each layer.

A total of 1087 independent reflexions was estimated visually by comparison with an intensity scale prepared from timed exposures of a suitable reflexion from the crystal. The values obtained from the various films for each layer were scaled together by means of the program SCALE,[2] using the weighting function $w=\{3+[(I-8)/6.5]^2\}^{-1}$. Initial scale factors between the layer lines were estimated from the exposure times.

UNIT CELL AND SPACE GROUP

According to a previous report,[1] potassium triformatostannate(II) crystallises in the orthorhombic system with $a=6.1_0$, $b=17.6_7$, $c=6.9_6$ Å, and space group No. 18 $—P22_12_1$. We find that the crystals are monoclinic with $a=6.15$, $b=17.7$, $c=7.0$ Å, $\beta=92°$, as estimated from rotation and Weissenberg photographs. In order to obtain accurate cell parameters, Guinier powder photographs were taken with $Pb(NO_3)_2$ as the internal standard ($CuK\alpha$ radiation, $\lambda=1.54050$ Å, $a_{Pb(NO_3)_2}=7.8566$ Å at $21°C$ [3]). Eighty two lines were indexed and a refinement of cell parameters based on these lines was made using the program POWDER.[4] The cell dimensions were found to be:

$$a = 6.1236\pm0.0005 \text{ Å}$$
$$b = 17.6481\pm0.0012 \text{ Å}$$
$$c = 6.9655\pm0.0005 \text{ Å}$$
$$\beta = 92.136°\pm0.006°$$
$$V = 752.2 \text{ Å}^3$$

The observed and calculated values of $\sin^2\theta$ are shown in Table 1.

The measured density (2.61 g·cm^{-3} by flotation in mixtures of sym-$C_2H_2Br_4$ and C_6H_6) agrees well with the calculated value of 2.58 g·cm^{-3}, assuming a unit cell content of 4 formula units. The systematically absent reflexions, $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$, indicate the monoclinic space group No. 14$—P2_1/c$.

STRUCTURE ANALYSIS AND REFINEMENT

As the linear absorption coefficient for $KSn(HCOO)_3$ is 331 cm^{-1}, the intensity data were corrected for absorption as well as polarization and Lorentz' effects, using the program DATAP2.[5] The absorption correction, however, was applied only after an approximate structure had been devised.

The positions of the tin atoms were found from the three-dimensional Patterson function $P(uvw)$ calculated by the program DRF,[6] using all the observed reflexions. The highest peaks in $P(uvw)$, excluding that at the origin, suggest that the tin atoms occupy the $4(e)$ position of $P2_1/c$ with $x\simeq0.25$, $y\simeq0.08$, $z\simeq0$. To obtain the sites of the potassium atoms a three-dimensional Fourier synthesis was calculated. Only F_0 values fulfilling the condition $0.3<|F_o|/|F_c|<3.0$ were used in order to avoid incorrect assignment of phases. Since the special coordinates of the tin atoms imply the existence of body-centering in the lattice, the Fourier showed an apparent eight-fold potassium position in the space group $I2/c$ which corresponds to two $4(e)$ positions in $P2_1/c$. Either of these is possible and the coordinate system was

Table 1. Guinier powder data for $KSn(HCOO)_3$. $CuK\alpha_1$ radiation, $\lambda = 1.54050$ Å.

h	k	l	$10^6 \sin^2\theta$ calc	$10^6 \sin^2\theta$ obs	I obs	h	k	l	$10^6 \sin^2\theta$ calc	$10^6 \sin^2\theta$ obs	I obs
0	2	0	7619	7594	w	1	2	3	136783	136725	vw
0	1	1	14149	14121	vvs	1	8	0	137756	137673	vvw
1	0	0	15843	15808	w	2	4	-2	138681	138667	vvw
1	1	0	17748	17703	m	3	0	0	142594	142583	w
0	2	1	19864	19808	m	3	1	0	144499	144427	w
1	2	0	23463	23390	vvw	2	4	2	146986	146988	vw
0	4	0	30478	30468	ms	1	8	-1	148963	148900	mw
1	3	0	32987	32946	vs	1	8	1	151039	151045	vw
1	2	-1	34670	34630	vvs	1	4	-3	153412	153293	m
1	2	1	36746	36709	vs	0	5	3	157827	157831	vw
1	3	-1	44194	44148	mw	3	2	-1	159344	159340	m
1	3	1	46270	46254	w	3	3	0	159738	159706	ms
0	0	2	48980	48946	ms	2	5	2	164130	164041	vvw
0	2	2	56599	56524	mw	3	2	1	165573	165573	m
0	5	1	59876	59776	s	2	7	-1	166883	166738	w
1	5	0	63465	63417	vs	2	1	-3	169256	169266	w
1	1	-2	64652	64612	s	1	9	0	170139	170159	w
2	1	0	65280	65229	vvw	2	7	1	171035	171006	w
0	3	2	66124	66035	vvw	2	6	-2	176778	176699	mw
1	0	2	66900	66815	m	1	5	3	176785	176699	mw
0	6	0	68578	68607	vs	2	8	0	185287	185229	mw
2	2	0	70944	70935	w	3	1	-2	187250	187228	vw
1	5	-1	74672	74577	m	0	0	4	195920	195848	w
2	1	-1	75448	75434	ms	1	6	3	197739		
2	1	1	79601	79551	vs	3	0	2	197803	197739	vw
0	6	1	80820	80809	w	0	1	4	197825		
1	3	2	84044	84010	s	3	3	-2	202489	202397	w
2	4	0	93853	93842	w	0	2	4	203540	203454	w
1	6	1	97702	97635	vw	1	1	-4	209516	209535	vvw
2	4	-1	104022	103928	w	3	3	2	214947	214910	w
2	0	-2	108202	108051	vw	1	10	1	219615	219504	vw
1	7	0	109183	109142	w	1	9	2	221195	221060	vw
0	1	3	112110	112087	ms	1	3	-4	224755	224655	vvw
2	0	2	116507	116440	m	3	5	-2	232967	232858	w
0	6	2	117556	117514	ms	2	8	2	238420	238436	vvw
2	5	-1	121166	121105	w	0	11	1	242736	242663	vvw
0	8	0	121912	121903	mw	1	8	-3	244847	244921	w
2	2	2	124127	124082	vvw	2	0	-4	250990	250975	w
2	5	1	125318	125260	m	1	10	-2	253236	253259	vw
2	3	-2	125346	125260	m	4	1	-1	263498	263506	vvw
1	2	-3	130554	130549	vw	0	6	-4	264496	264444	vw
2	6	0	131951	131944	w	3	8	-1	273637	273548	w
2	3	2	133651	133588	vvw	3	9	0	296890	296831	vvw

specified by placing the potassium atoms in $4(e)$ with $x \simeq 0.68$, $y \simeq 0.32$, $z \simeq 0.17$.

The positions of the tin and potassium atoms, their isotropic temperature factors and the initial scale factors for the layer lines were then refined by the full matrix least-squares program LALS,[7] giving an R value of 0.25 $(R = \sum ||F_o| - |F_c||/\sum |F_o|)$. A subsequent Fourier calculation, using $(F_o - F_c)$ as input values, revealed the positions of all the carbon and oxygen atoms. An initial refinement of the parameters for all the atoms in the unit cell gave an R value of 0.14.

At this stage the preliminary F_o data were replaced by absorption-corrected values. Unobserved reflexions, which were assigned an intensity one half of the lowest observable value, were also introduced but were not included in the subsequent refinements. Three cycles of isotropic refinement lowered the residual to 0.098. The final refinement was carried out using anisotropic temperature factors, an overall scale factor, scattering factors for Sn, K^+, O and C according to Cromer and Waber [8] and the structure factor weighting scheme due to Cruickshank [9] $(w = (a + F_o + cF_o^2 + dF_o^3)^{-1}$ with $a = 26$, $c = 0.01$, and $d = 0$. After four cycles all parameter shifts became less than 1 % of the

Table 2. Observed and calculated structure factors for KSn(HCOO)₃. The columns are
k, $|F_o|$ and F_c, respectively. Unobserved reflexions are indicated by a dash.

```
  0 K 0            8  34 -33     11   -  -3      4  20  19      2  83 -86      5  21 -21
 2  68  40         9  36 -33     12   -   4      5  51 -43      3 139 -151     6  20 -19
 4 127 -108       10  29  26     13  21 -25      6   -   4      4   8   3      7  35  30
 6 190 -189       11   -  -6                     7  41  38      5  35 -31      8   -  -7
 8 141 -140       12  73  67       1 K -6        8  39  34      6  32  28      9  32  30
10  62  57        13  19  17      0  41 -45      9 108 110      7  52  50     10   -   8
12 114 118        14  42  38      1  15 -15     10  56 -50      8  21 -17     11   -  10
14  39  40        15   - -10      2  13 -12     11  59  47      9 112 111     12  18  14
16  12 -13        16  32 -31      3  70 -77     12  28 -27     10   -   0     13  12 -10
18  54 -56        17  10  10      4  23  22     13  55 -54     11  45  41     14  10  10
20  29 -26        18  34 -33      5  47 -48     14   -   8     12  12  10     15  37 -43
22  14  17        19   -   4      6  27  25     15  40 -40     13  39 -38     16   -  -0
                  20  16 -16      7  43  44     16   -  -3     14  18 -17
  0 K 1                          8  21  17     17  32 -31     15  58 -62       1 K 7
 1 128 142          0 K 5         9  52  51     18  26  23     16  11  12      1   -  10
 2  56  58         1  68  70     10  12 -12     19  16  12     17  30 -30      2  46 -47
 3  10  -7         2   -   2     11  26  24     20   -   8     18   -  -3      3  17  15
 4  11 -10         3  28  25     12  32 -29     21  31  34     19  22  22      4  41 -38
 5 134 -125        4  35  35     13  16 -13     22   -   0     20   -  -5      5  29 -26
 6  94  85         5  92 -100    14   -  -2                    21  27  29      6   -  -7
 7 194 -152        6   -   0     15  38 -43       1 K -1       22   -   2      7  14 -14
 8  16 -13         7  42 -70     16   -  -1      1  71 -76                     8  29  27
 9  51  42         8  23 -21                     2 149 -167      1 K 3         9   -   7
10  57 -50         9  19  18       1 K -5        3  60 -53      1   -   7     10  45  40
11  78  76        10   -   6      1  28 -30      4  89 -84      2  68 -70     11   -   3
12  13  12        11  47  46      2  82 -88      5 109 102      3   8  -5     12   -  -5
13  90  88        12  18 -19      3   -   0      6  25  18      4 117 -128    13  12  11
14   -  -8        13  55  51      4  44 -46      7  52  45      5   -  -2
15   -   1        14   -   7      5  25  24      8 111 108      6  32  31       1 K 8
16   -  -5        15   -  -2      6  12 -10      9   -  -5      7  41 -37      0  34  32
17  55 -56        16  10  10      7  29  29     10  87  85      8  74  75      1  21 -15
18  15  14        17  32 -34      8  47  46     11   -  -5      9   -   0      2   -  11
19  44 -43        18   -   0      9   -   7     12   -  -1     10  45  42      3  33 -33
20   8  -6                       10  71  71     13  18 -13     11   -   4      4  16 -14
21   -  -3          0 K 6        11  33 -30     14  70 -72     12  12  10      5  11  10
22   -   0         0  80  85     12   -  -2     15  20 -20     13  17  12      6   -  -7
                   1   -   7     13  15 -15     16  58 -60     14  43 -42      7  12  11
  0 K 2            2  25  26     14  46 -46     17  19  22     15   -   3      8  22 -23
 0 127 148         3  11  13     15   -  -1     18   -  -1     16  46 -49      9  26  26
 1  14 -13         4  44 -45     16  29 -28     19   -  -6     17   -  -4
 2  73  73         5  13  10     17   -   6     20  35  37     18  10  12       2 K -7
 3  66 -58         6  44 -44     18  10  -9     21   -   3     19   6  -5      1  37 -40
 4  29 -29         7  16 -15                    22  23  26     20  18  17      2  33  33
 5   9   9         8  40 -39       1 K -4                      21   -  -4      3   -   5
 6 160 -195        9   -  -8      0  31 -30       1 K 0                        4  16  20
 7  35 -34        10  36  34      1  46 -49      2  25 -17       1 K 4         5  27  27
 8  54 -46        11   - -12      2  50 -52      3 178 -165     0   8  -6      6   -   6
 9  32  26        12  51  47      3  92 -101     4  70  57      1  44 -44      7  39  36
10  65  59        13   -   2      4  17  16      5 169 -158     2   -   2      8  13 -14
11   -   6        14  13  11      5  48 -48      6  53 -43      3  99 -107     9   -   9
12  96  92        15  20  19      6  65  69      7  77  76      4  24  21     10  32 -30
13  12 -12        16  12 -13      7  34  55      8  40  35      5  37 -30     11  39 -37
14  59  54        17   -   5      8   -   6      9 106 105      6  30 -29     12   -   2
15  22  20                        9  65  64     10   -  -5      7  16  12     13  16 -16
16  31 -36          0 K 7        10   -   7     11  58  59      8   -   5
17   -   4         1  50  48     11  46  43     12   -  -2      9  79  91       2 K -6
18  50 -55         2  20  22     12  26 -29     13  11  -9     10   -  -3     0  59 -67
19  12 -12         3   -   5     13  31 -29     14   -   0     11  33  29      1  13 -12
20  23 -24         4   -   0     14  34 -31     15  67 -72     12   -  -2      2  31 -30
21   -   4         5  46 -45     15  54 -57     16   -  -5     13  33 -30      3  31  31
22   8  12         6  14  12     16  12  11     17  33 -32     14  19  21      4  34  34
                   7  36 -36     17  24 -21     18   -   7     15  33 -30      5  32  33
  0 K 3            8   -  -5     18  21  21     19  27  27     16   -  -3      6  40  42
 1 152 178         9   -  -6     19  16  15     20   -  -1     17  22 -20      7  25 -26
 2  45  46        10  27 -25     20   -  -1     21  23  21     18  12 -11      8  35  34
 3  50 -44        11  27  25                    22   -  -1     19   8   8      9  14 -11
 4   -   0        12   -   2       1 K -3                      20   -   0     10  21 -20
 5  80 -85        13  29  31      1  53 -56       1 K 1                       11  23 -20
 6   9  10        14   9   9      2  89 -95      1  11   0       1 K 5        12  46 -42
 7 121 -125                      3  26  24      2 118 -123     1  47  47     13   -   2
 8  29 -28          0 K 8        4 173 -186     3  16  14      2  57 -64     14  13 -13
 9  37 -11         0  21  20     5   7   8      4  50 -46      3  31 -23     15  18  20
10   -  -4         1   -  -2     6   -   0      5   8   1      4  58 -64     16  10  12
11  90  88         2  26  24     7  34  34      6  57 -51      5   -   5
12   -  -6         3  22  24     8 107 111      7   -  -5      6   -   7       2 K -5
13  77  74         4  14 -15     9  35  31      8  98  81      7  31 -30     1  55 -55
14   -   8         5  17  17    10  67  61      9  24  19      8  41  40      2  22  23
15   -   0         6  41 -38    11  37 -33     10 106 110      9  29 -27      3  27 -26
16  11  12         7   - -11    12  34  26     11  51 -51     10  57  59      4  22  24
17  33 -34         8  11 -10    13  15 -13     12  28 -28     11  20  19      5  85  90
18   -   0         9   9  -9    14  54 -56     13   -   7     12   -  -3      6   -  -7
19  41 -46        10  13  16    15  15 -14     14  46 -43     13  13  11      7  44  41
20   -  -4                      16  45 -44     15   -   4     14  36 -35      8  15 -13
21   -   1          1 K -7      17   -   9     16  46 -47     15   -   8      9  12 -10
                   1  21 -23    18   -  -1     17   -   6     16  31 -30     10  24 -24
  0 K 4            2  48 -48    19  17  16     18  13  -9     17   -   1     11  26 -25
 0  99 105         3  18 -18    20  21  22     19  11   9     18   -  -2     12   -  -6
 1  62  63         4  50 -51    21   -  -1     20  36  36                    13  47 -44
 2  68  68         5  43  42                   21   -   2       1 K 6        14  20  20
 3   8  -4         6   -  -1      1 K -2       22  23  25      0  13  11     15   -  -4
 4  54 -54         7  18  18     0  31 -27                    1   9   7     16  15  16
 5  17  16         8  42  41     1 122 -131      1 K 2        2  13  13     17  26  31
 6 104 -108        9   -  -2     2  19  16      0 114 -122    3  59 -60     18   -   3
 7  15  12        10  33  30     3 101 -105     1  97 -101    4  10 -10
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Table 2. Continued.

2 K -4			3	10	-5	4	52	52	4	13	-16	3 K -1			4	7C	72
0	80	-84	4	81	68	5	21	18	5	30	26	1	7	10	5	16	12
1	52	48	5	41	33	6	96	109	6	18	-19	2	70	82	6	-	-6
2	49	-46	6	99	97	7	-	-6	7	30	-26	3	17	17	7	24	-20
3	34	33	7	9	-4	8	40	38	8	26	-23	4	131	137	8	75	-83
4	56	55	8	98	97	9	19	20	9	51	-45	5	23	-21	9	-	-6
5	-	3	9	-	0	10	28	-24	10	-	4	6	26	-19	10	46	-43
6	77	79	10	59	-57	11	-	4	11	24	-19	7	48	-39	11	27	24
7	-	7	11	13	12	12	54	-52	12	30	28	8	112	-106	12	-	0
8	37	33	12	80	-80	13	-	-8	13	16	16	9	37	30	13	-	1
9	32	-31	13	25	-22	14	46	-48				10	61	-59	14	44	44
10	47	-43	14	20	-17	15	-	-7	3 K -5			11	-	0	15	-	-10
11	18	-18	15	14	13	16	28	27	1	21	24	12	10	-9	16	43	45
12	73	-70	16	-	7	17	8	-9	2	73	78	13	12	10	17	-	4
13	19	16	17	8	-7	18	30	34	3	-	7	14	61	62	18	-	-4
14	-	-7	18	41	44	19	-	3	4	52	56	15	-	7	19	8	-11
15	-	2	19	-	-4				5	37	-41	16	47	49			
16	16	15	20	21	19	2 K 5			6	16	14	17	15	-15	3 K 4		
17	14	14	21	-	4	1	71	-73	7	20	-20	18	-	-1	0	15	12
18	34	35				2	13	-12	8	50	-49	19	-	-1	1	49	79
19	-	-1	2 K 1			3	-	2	9	19	14	20	21	-23	2	-	6
			1	115	-146	4	55	-57	10	73	-66	21	-	-1	3	79	82
2 K -3			2	14	-13	5	61	65	11	-	9				4	-	0
1	102	-110	3	25	-21	6	-	1	12	-	7	3 K 0			5	29	25
2	8	-3	4	-	3	7	52	53	13	28	26	1	74	75	6	-	-9
3	-	-4	5	152	164	8	20	19	14	34	33	2	20	-15	7	17	-12
4	64	65	6	-	-2	9	-	7	15	-	-3	3	135	129	8	-	7
5	86	80	7	99	97	10	-	9	16	22	24	4	28	-21	9	70	-75
6	-	3	8	39	-24	11	41	-44				5	65	63	10	17	-15
7	78	76	9	13	-11	12	11	13	3 K -4			6	14	-11	11	27	-28
8	32	-30	10	16	12	13	18	-19	0	12	10	7	59	-55	12	-	3
9	35	32	11	62	-62	14	-	2	1	17	16	8	57	-51	13	25	25
10	-	1	12	9	8	15	-	-4	2	21	23	9	90	-90	14	-	-2
11	76	-71	13	67	-67	16	15	-16	3	81	87	10	40	40	15	32	31
12	16	-12	14	-	2	17	23	26	4	-	1	11	44	-44	16	-	-1
13	54	-50	15	17	-17				5	51	52	12	17	15	17	17	17
14	-	-1	16	-	3	2 K 6			6	49	-51	13	23	20	18	-	6
15	-	3	17	55	60	0	60	-64	7	61	-64	14	-	-7			
16	13	12	18	-	-6	1	-	-6	8	-	2	15	63	66	3 K 5		
17	28	24	19	27	25	2	21	-21	9	51	-54	16	-	0	1	15	-12
18	-	-3	20	-	1	3	16	-14	10	-	8	17	28	27	2	44	42
19	31	31	21	-	-1	4	35	37	11	42	-39	18	-	-6	3	10	9
20	-	4	22	-	0	5	-	3	12	18	17	19	20	-20	4	62	62
						6	39	40	13	31	28	20	8	-8	5	20	-18
2 K -2			2 K 2			7	-	-9	14	17	15				6	-	3
0	76	-74	0	136	-155	8	29	29	15	57	58	3 K 1			7	-	12
1	21	19	1	37	37	9	24	23	16	11	-11	1	32	32	8	49	-46
2	106	-105	2	67	-68	10	33	-31	17	18	18	2	143	160	9	22	22
3	6	4	3	40	-34	11	-	1	18	9	-10	3	19	-16	10	32	-29
4	60	61	4	81	83	12	44	-46				4	67	69	11	-	-9
5	12	-11	5	65	-63	13	-	-4	3 K -3			5	14	-13	12	-	-12
6	125	133	6	92	96	14	-	-7	1	57	60	6	46	40	13	-	4
7	14	-16	7	35	32	15	-	-4	2	90	94	7	17	-15	14	29	30
8	25	17	8	73	80				3	29	-28	8	90	-84	15	9	-8
9	34	-30	9	11	11	2 K 7			4	97	104	9	-	6	16	20	22
10	-	-8	10	62	-60	1	41	-40	5	-	3	10	102	-108			
11	-	-9	11	17	14	2	16	-14	6	9	-6	11	-	-1	3 K 6		
12	72	-74	12	71	-74	3	18	-17	7	45	-46	12	-	8	0	13	12
13	10	11	13	10	10	4	-	-5	8	68	-62	13	16	16	1	16	14
14	50	-51	14	34	-36	5	56	52	9	31	-26	14	48	50	2	15	-13
15	19	19	15	16	-16	6	-	0	10	68	-64	15	-	0	3	40	38
16	30	30	16	19	18	7	39	37	11	31	30	16	44	47	4	-	2
17	-	7	17	10	-10	8	-	2	12	21	-18	17	-	-9	5	32	28
18	46	47	18	45	49	9	-	-4	13	18	18	18	11	10	6	-	7
19	11	-9	19	-	7	10	19	19	14	49	49	19	-	0	7	32	-32
20	12	8	20	17	17	11	18	-17	15	-	-1	20	29	-33	8	-	-3
21	-	-5	21	-	-4	12	-	0	16	44	40	21	-	0	9	34	-32
									17	-	-1				10	-	4
2 K -1			2 K 3			2 K 8			18	-	3	3 K 2			11	16	-15
1	101	-112	1	79	-83	0	35	-34	19	12	-15	0	33	-30	12	-	4
2	58	63	2	30	-28	1	8	9				1	36	35	13	12	12
3	15	12	3	19	16	2	14	-15	3 K -2			2	7	7			
4	81	-67	4	23	18	3	21	-21	0	37	37	3	99	101	3 K 7		
5	113	108	5	58	55	4	14	13	1	93	101	4	12	10	1	-	-5
6	46	39	6	20	-18	5	16	-13	2	-	0	5	78	78	2	43	39
7	103	97	7	80	81	6	28	31	3	121	137	6	29	-26	3	-	1
8	22	18	8	-	1	7	-	8	4	18	-17	7	50	-46	4	18	16
9	13	6	9	18	18				5	68	62	8	24	20	5	-	6
10	36	-32	10	34	31	3 K -7			6	12	-29	9	84	-86	6	-	8
11	105	-108	11	88	-88	2	35	33	7	44	-39	10	-	5	7	-	6
12	13	11	12	16	-13	3	10	10	8	-	-2	11	38	-32	8	21	-20
13	58	-58	13	40	-40	4	49	48	9	110	-108	12	-	-1	9	-	-2
14	-	-7	14	-	6	5	25	-24	10	18	16	13	13	10	10	26	-29
15	-	-3	15	-	-3	6	-	-9	11	54	-53	14	14	15			
16	-	5	16	-	-11	7	27	-23	12	19	18	15	54	59	3 K 8		
17	46	47	17	34	34	8	39	-36	13	49	48	16	15	-16	0	14	-15
18	-	4	18	9	-9	9	-	2	14	23	23	17	18	19	1	11	12
19	44	45	19	32	36	10	23	-22	15	42	40	18	-	-6	2	-	1
20	-	-6	20	5	6	11	7	9	16	20	-19	19	12	-12	3	22	24
21	-	0							17	32	29	20	-	3	4	-	4
22	-	0	2 K 4			3 K -6			18	16	-16						
			0	74	-75	0	57	61	19	10	-9	3 K 3			4 K -7		
2 K 0			1	26	-25	1	35	33	20	-	-6	1	18	15	5	19	-16
1	43	-50	2	86	-91	2	-	3				2	82	81	6	-	1
2	76	-66	3	20	-19	3	59	62				3	19	-16	7	30	-31

standard deviations and the R value converged to 0.075 for observed reflexions (0.094 including 347 unobserved reflexions).

Table 2. Continued.

8	19	20	2	54	62	17	34	-33	4	K	6	15	-	1	17	6	7
9	-	-4	3	33	-32	18	-	-3	0	45	41	16	18	-23			
			4	28	-24	19	17	-19	1	22	21					5 K 2		
	4 K -6		5	-	-1.				2	18	14		5 K -2		0	18	-14
0	41	43	6	104	-107		4 K 2		3	-	8	0	19	16	1	18	-15
1	-	-6	7	-	-1	0	118	124	4	25	-20	1	32	-34	2	6	4
2	21	21	8	23	-21	1	13	-12	5	-	-1	2	19	-33	3	74	-84
3	41	-42	9	47	45	2	28	23	6	33	-32	3	64	-74	4	6	4
4	13	-12	10	21	18	3	9	-9	7	-	10	4	13	10	5	44	-45
5	35	-32	11	-	1	4	48	-43	8	-	-10	5	23	-19	6	7	c
6	56	-51	12	49	51	5	9	6	9	16	-17	6	29	28	7	33	32
7	29	27	13	17	-16	6	54	-46	10	10	11	7	26	20	8	-	0
8	15	-16	14	30	33	7	-	2	11	-	-3	8	-	1	9	52	47
9	12	16	15	-	-7	8	61	-59				9	54	47	10	9	-9
10	17	16	16	24	-23	9	20	19		4 K 7		10	-	-4	11	30	30
11	22	19	17	-	-12	10	36	34	1	19	19	11	34	32	12	-	-3
12	26	30	18	25	-27	11	-	-3	2	-	2	12	11	-11	13	7	-2
			19	-	2	12	39	41	3	-	9	13	26	-24	14	-	0
	4 K -5					13	18	-18	4	-	9	14	19	-17	15	38	-43
1	50	54		4 K -1		14	17	15	5	27	-31	15	31	-33	16	-	3
2	28	-31	1	66	82	15	-	2	6	-	2	16	12	13			
3	15	12	2	32	-36	16	10	-5	7	17	-19	17	10	-13		5 K 3	
4	19	-20	3	33	-30	17	-	-1							1	-	1
5	53	-54	4	15	-15	18	20	-23		5 K -6			5 K -1		2	49	-47
6	-	-8	5	45	-40				3	32	-30	1	21	-25	3	22	20
7	58	-54	6	15	-7		4 K 3		4	16	14	2	41	-48	4	38	-35
8	25	22	7	70	-59	1	58	57	5	17	-13	3	8	7	5	19	-14
9	-	4	8	22	20	2	18	15	6	22	20	4	83	-78	6	9	-7
10	38	36	9	21	-20	3	15	-13	7	13	10	5	17	16	7	-	-4
11	28	23	10	33	33	4	22	-20	8	23	23	6	22	19	8	43	42
12	-	-5	11	53	56	5	51	-48	9	28	36	7	16	15	9	10	6
13	39	39	12	11	-11	6	26	26				8	51	53	10	47	44
14	17	-20	13	46	46	7	49	-46		5 K -5		9	-	5	11	12	-13
15	-	2	14	10	-10	8	-	6	1	17	-16	10	35	36	12	11	-13
			15	-	-2	9	-	5	2	49	-51	11	19	-18	13	-	2
	4 K -4		16	9	-21	10	22	-20	3	18	-17	12	14	13	14	21	-24
0	85	96	17	22	-21	11	43	42	4	41	-36	13	7	-6	15	5	7
1	16	-15	18	-	-1	12	-	4	5	42	40	14	32	-33			
2	-	6	19	26	-33	13	36	38	6	-	-3	15	-	-5		5 K 4	
3	37	-38				14	-	-5	7	14	12	16	30	-34	0	11	-9
4	35	-36		4 K 0		15	-	-1	8	40	30	17	11	12	1	37	-33
5	11	-12	1	15	11	16	-	-4	9	-	-4				2	12	-11
6	46	-45	2	42	46	17	25	-29	10	34	32		5 K 0		3	48	-47
7	12	12	3	41	-35				11	7	-9	1	30	-36	4	8	-6
8	29	-28	4	50	-43		4 K 4		12	-	2	2	14	11	5	17	-16
9	31	27	5	12	-14	0	34	30				3	70	-81	6	20	17
10	30	26	6	81	-84	1	10	-9		5 K -4		4	20	15	7	16	13
11	24	22	7	24	21	2	40	35	0	25	-26	5	27	-26	8	8	-9
12	56	52	8	35	-33	3	-	-1.	1	8	-6	6	17	-11	9	45	44
13	17	-15	9	13	11	4	15	-12	2	20	-21	7	26	23	10	8	8
14	-	8	10	32	29	5	-	3	3	50	-51	8	16	15	11	19	17
15	23	-21	11	-	4	6	62	-60	4	28	26	9	63	72	12	-	3
16	18	-11	12	54	56	7	-	-9	5	40	-36	10	21	-20	13	17	-19
17	6	-8	13	-	9	8	20	-18	6	20	19	11	20	21	14	-	-3
			14	30	31	9	-	-3	7	43	41	12	11	-11			
	4 K -3		15	25	-29	10	19	17	8	11	12	13	30	-28		5 K 5	
1	62	68	16	25	-24	11	-	2	9	38	32	14	10	11	1	-	3
2	30	-32	17	-	-4	12	29	26	10	15	-11	15	31	-30	2	38	-32
3	15	14	18	29	-29	13	-	-4	11	24	18	16	-	0	3	-	-1
4	66	-72	19	12	14	14	26	27	12	22	-20	17	16	-20	4	54	-47
5	74	-76				15	11	12	13	12	-11				5	-	3
6	15	14		4 K 1		16	14	-15	14	-	-7		5 K 1		6	-	7
7	61	-61	1	56	61							1	10	-11	7	-	-4
8	31	30	2	26	-25		4 K 5			5 K -3		2	55	-63	8	32	32
9	-	8	3	27	24	1	49	47	1	27	-27	3	21	-19	9	9	-6
10	-	13	4	-	6	2	-	7	2	53	-57	4	48	-44	10	20	16
11	40	34	5	77	-78	3	11	-9	3	-	3	5	29	26	11	-	1
12	19	19	6	25	-21	4	13	12	4	45	-47	6	-	1			
13	51	48	7	78	-72	5	26	-23	5	19	17	7	17	16		5 K 6	
14	16	-16	8	-	2	6	-	3	6	9	-8	8	37	35	0	12	-13
15	-	-4	9	20	20	7	42	-42	7	20	18	9	12	-11	1	21	-10
16	22	-22	10	25	24	8	-	-8	8	48	40	10	49	55	2	9	5
17	21	-21	11	35	35	9	-	-9	9	15	16	11	-	-5	3	28	-27
18	-	6	12	11	-10	10	-	4	10	59	55	12	-	-5	4	7	-5
			13	40	41	11	33	33	11	30	-28	13	-	-4	5	16	-16
	4 K -2		14	-	6	12	8	-10	12	-	-5	14	30	-32	6	10	-10
0	64	65	15	-	6	13	20	20	13	7	-7	15	-	-2	7	10	11
1	25	-26	16	-	-5	14	-	-4	14	31	-30	16	24	-28	8	-	1

As a check on the refinement results, a three-dimensional $(F_o - F_c)$ synthesis was calculated. The largest disagreements, about 2 electrons/Å^3, appeared in the vicinity of the tin and potassium atoms. These are probably due to diffraction effects and to the fact that the atomic scattering factors used are not strictly applicable to the bonded atoms in this structure.

The final atomic positions and thermal parameters are shown in Table 3, while Table 2 contains a list of the observed and calculated structure factors. The interatomic distances and angles, listed in Table 4, were calculated using the program DISTAN.[10]

Table 3. Final atomic parameters for $KSn(HCOO)_3$. The anisotropic temperature factor is
$\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*U_{12}+hla^*c^*U_{13}+klb^*c^*U_{23})]$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	0.25874(16)	0.41729(5)	0.49043(13)	0.0348(8)	0.0340(5)	0.0324(6)	0.0042(8)	0.0177(8)	0.0079(8)
K	0.6813(6)	0.31952(21)	0.1738(5)	0.0325(20)	0.0498(18)	0.0307(15)	0.0197(29)	0.0069(24)	0.0074(27)
O_1	0.3168(18)	0.3006(6)	0.4023(16)	0.041(7)	0.031(5)	0.055(6)	−0.008(9)	0.026(10)	−0.011(9)
O_2	−0.0261(20)	0.2731(7)	0.4706(16)	0.045(8)	0.043(6)	0.053(7)	−0.008(10)	0.017(11)	0.005(10)
O_3	0.6124(19)	0.4187(6)	0.5317(14)	0.051(7)	0.029(5)	0.036(5)	0.014(9)	−0.010(9)	−0.016(8)
O_4	0.5568(21)	0.3530(8)	0.7943(18)	0.055(8)	0.057(8)	0.057(7)	0.016(12)	0.017(11)	−0.049(12)
O_5	0.3595(21)	0.4425(7)	0.2066(15)	0.065(8)	0.046(6)	0.035(6)	−0.014(11)	−0.006(11)	0.007(9)
O_6	0.0238(25)	0.4162(8)	0.1232(23)	0.061(10)	0.064(9)	0.085(10)	0.008(14)	−0.031(15)	0.007(15)
C_1	0.1499(28)	0.2558(9)	0.4183(19)	0.055(11)	0.036(7)	0.026(6)	−0.030(14)	−0.009(13)	−0.009(11)
C_2	0.6747(25)	0.3877(9)	0.6926(22)	0.032(9)	0.045(8)	0.039(8)	−0.003(13)	−0.011(12)	−0.010(13)
C_3	0.2071(28)	0.4407(9)	0.0830(24)	0.032(11)	0.041(8)	0.050(9)	0.020(14)	−0.006(14)	0.006(13)

Table 4. Distances (Å) and angles (°) in the $Sn(HCOO)_3^-$ ion (standard deviations in parentheses).

Bond		Angle	
$Sn-O_1$	2.182(10)	O_1-Sn-O_3	82.9(5)
$Sn-O_3$	2.174(11)	O_1-Sn-O_5	83.2(5)
$Sn-O_5$	2.139(11)	O_3-Sn-O_5	78.4(5)
C_1-O_1	1.300(20)		
C_1-O_2	1.190(20)	$O_1-C_1-O_2$	126.5(1.5)
C_2-O_3	1.292(18)		
C_2-O_4	1.199(20)	$O_3-C_2-O_4$	124.3(1.5)
C_3-O_5	1.246(21)		
C_3-O_6	1.245(23)	$O_5-C_3-O_6$	120.8(1.6)

Other distances in $KSn(HCOO)_3$.

		$K-O_6$	2.736(16)
		$K-O_4$	2.787(13)
$Sn-O_2$	3.085(12)	$K-O_2$	2.808(12)
$Sn-O_4$	2.968(13)	$K-O_1$	2.809(12)
$Sn-O_6'$	2.888(16)	$K-O_2$	2.841(12)
$Sn-O_3'$	3.006(10)	$K-O_5$	2.946(13)
		$K-O_3$	3.088(10)
		$K-O_4$	3.256(14)

DISCUSSION OF THE STRUCTURE

The structure of potassium triformatostannate(II) can be described in terms of the close-packing of discrete $Sn(HCOO)_3^-$ ions and potassium ions. There is no evidence for the formation of chains (*cf.* $2KSnF_3 \cdot H_2O$ [11]), layers
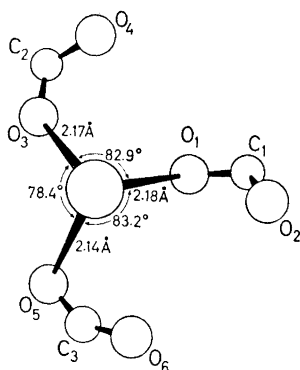
Fig. 1. The configuration of the
Sn(HCOO)$_3^-$ ion.

(*cf.* tetragonal SnO [12],[13]) or groups (as in Sn$_2$OSO$_4$[14],[15]).* The shortest distance between a tin atom and an oxygen atom (O$_3'$) belonging to a neighbouring anion is 3.00$_6$ Å (see Fig. 2).

Fig. 1 shows the configuration of the Sn(HCOO)$_3^-$ ion. The tin atom is coordinated pyramidally by three oxygen atoms (O$_1$, O$_3$, O$_5$) of three formate groups. The Sn—O distances, which are similar to those in Sn$_2$OSO$_4$, suggest that the tin-oxygen bonds are essentially covalent in character. This is in agreement with Mössbauer studies,[16] which have shown that the Mössbauer chemical shift for the tin atom in KSn(HCOO)$_3$ is +1.03 ±0.05 mm/sec (relative to α-Sn), compared with a calculated value of +5.6 mm/sec for the hypothetical Sn^{2+} ion. The environment of the tin atom is completed by the remaining oxygen atoms (O$_2$, O$_4$, O$_6$) of the three formate groups in the anion, together with one oxygen atom (O$_3'$) from a neighbouring ion. These four oxygen atoms, which are at distances between 2.88$_8$ Å and 3.08$_5$ Å, are not bonded directly to the tin atom.

The present work confirms the reported results of infrared studies [17] on a number of triformato- and triacetatostannates(II). The observed shifts of ν_{sym}(OCO) and ν_{as}(OCO), compared with ionic formates and acetates, have been interpreted in terms of the effect on the C—O bonds of unidentate complexing.

From the point of view of tin-nearest-neighbour atoms, the Sn(HCOO)$_3^-$ ion is similar to the trichlorostannate(II) ion in KCl·KSnCl$_3$·H$_2$O.[18] The latter ion also has a pyramidal configuration, with Sn—Cl bond lengths of 2.54, 2.54, 2.63 Å and Cl—Sn—Cl angles of 87.7, 87.7, 90.8 degrees. Three more distant chlorine atoms (at 3.17, 3.35, 3.35 Å) make up a distorted octahedron around the tin.

A study [19] of the far-infrared spectra of a number of SnX$_3^-$ derivatives, including KSn(HCOO)$_3$, has suggested that in compounds of this type there are significant distortions of the tin environment, these distortions being the result of lengthening one or two of the tin-nearest-neighbour bonds. Similarly,

* Sn$_2$OSO$_4$ contains clusters of four oxygen atom tetrahedra sharing edges, with a tin atom at the centre of each tetrahedron. The shorter Sn—O distances within these groups range from 2.12 Å to 2.47 Å.

high Mössbauer quadrupole splittings have been associated with compounds known to have or suspected of having considerably distorted tin environments. $KSn(HCOO)_3$ has a comparatively high splitting of 1.95 mm/sec. A large distortion has certainly been found in $2KSnF_3 \cdot H_2O$, but in the case of potassium triformatostannate(II) it is impossible to say, from the Sn—O distances, whether or not the tin-oxygen pyramid is distorted. However, if any differences in the bond lengths do exist they must be quite small, certainly no greater than 2—3 %. Although the far-infrared spectrum could be accounted for by a distortion of this magnitude, it seems unlikely that a completely satisfactory explanation of the Mössbauer data for $KSn(HCOO)_3$ can be obtained from a consideration of the bond lengths alone.

The C—O bonds and angles in $KSn(HCOO)_3$ are comparable to those found in other compounds containing the formate group. Sodium formate [20] has two equivalent C—O distances of 1.27 Å and an O—C—O angle of 124°. Pauling and Brockway [21] found values of 1.29 Å and 125° for the dimer of formic acid. A more recent investigation of ammonium formate [22] has shown the C—O bond lengths to be 1.237 and 1.246 Å and the angle 126.3°. In the dimer and the ammonium salt the oxygen atoms are involved in hydrogen-bonding.
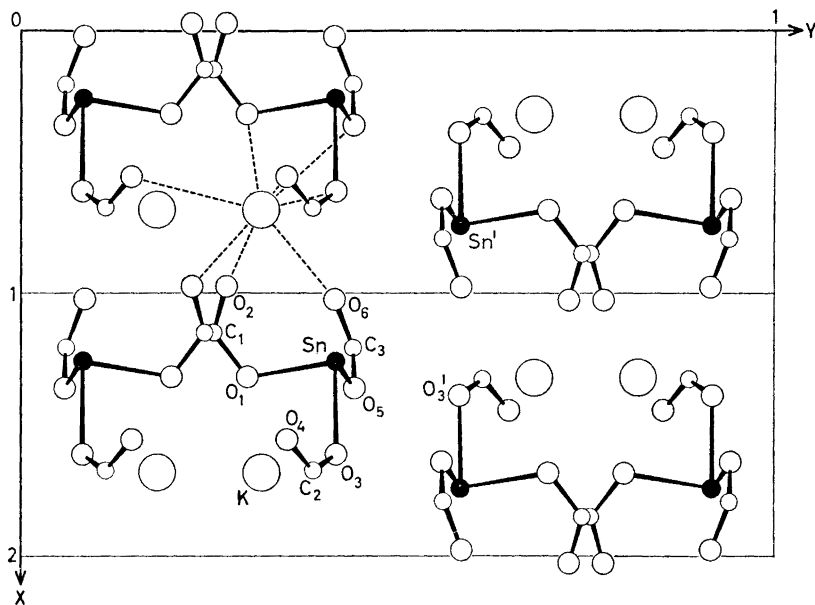
Fig. 2. The structure of $KSn(HCOO)_3$ viewed along the z axis.

For the groups $O_1C_1O_2$ and $O_3C_2O_4$, the differences between the C—O distances appear to suggest that the two bonds are not equivalent, as would be expected for coordination through only one oxygen atom. The group $O_5C_3O_6$, however, does not show this behaviour. In the lattice this group lies

in the neighbourhood of a region occupied by the $5s^2$ lone-pair electrons of two $Sn(HCOO)_3^-$ ions (see Fig. 2) and the distance between O_6 and Sn' is considerably greater than that between O_3' and Sn. This might suggest that there is some degree of repulsion between the Sn' lone-pair and the $O_5C_3O_6$ group, thus influencing the bonds within the group. It must be stressed, however, that no great significance can be attached to arguments based on the bond lengths in view of the magnitude of the standard deviations.

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