

Fig. 9 (cont.). (c) Hypothetical structure $R_{11}X_{17}$.

restrictions that all edges of the pentagons should be long, that the rectangles should have two long edges, and that the triangles have only one long edge. The space group for the structure in Fig. 9(b) is $Amam (D_{2h}^{17})$, $Z=100$; the composition is R_2X_3 . In Fig. 9(c) the arrangement of the pentagons along the X axis is like the arrangement of the VF polyhedra in

β - Mg_2Al_3 along the [110] axis (Samson, 1968). The composition is $R_{11}X_{17}$, $Z=224$, space group $Amam$. Since there is no obvious way to divide these structures into strips, the derivation of code names becomes arbitrary and cumbersome. It is clear that many more structures of this type with larger cells could be derived. Both the P & S and the K coding scheme are clearly inadequate to describe these structures.

References

- KRIPYAKEVICH, P. I. (1970). *Kristallografiya*, **15**, 690. [*Sov. Phys. Crystallogr.* (1971). **15**, 596.]
 KRIPYAKEVICH, P. I. & YARMOLYUK, YA. P. (1970). *Dop. Akad. Nauk Ukr. RSR*, **A32**, 948.
 KRIPYAKEVICH, P. I. & YARMOLYUK, YA. P. (1971). *Всесоюзная Конференция по Кристаллохимии Интерметаллических Соединений, Тезисы докладов, Львов*, s. 6.
 MANOR, P. C., SHOEMAKER, C. B. & SHOEMAKER, D. P. (1972). *Acta Cryst.* **B28**, 1211.
 PEARSON, W. B. & SHOEMAKER, C. B. (1969). *Acta Cryst.* **B25**, 1178.
 SAMSON, S. (1968). In *Structural Chemistry and Molecular Biology*, p. 687. Edited by A. RICH & N. DAVIDSON. San Francisco: Freeman.
 SHOEMAKER, C. B. & SHOEMAKER, D. P. (1969). In *Developments in the Structural Chemistry of Alloy Phases*, p. 117. Edited by B. C. GIESSEN. New York: Plenum Press.
 WELLS, A. F. (1968). *Acta Cryst.* **B24**, 50.
 YARMOLYUK, YA. P., KRIPYAKEVICH, P. I. & HLADYSHEVSKIY, E. I. (1970). *Kristallografiya*, **15**, 268. [*Sov. Phys. Crystallogr.* (1970). **15**, 226.]

Acta Cryst. (1972). **B28**, 2965

The Crystal Structure of Tin(II) Iodide

BY R. A. HOWIE, W. MOSER* AND I. C. TREVENA

Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

(Received 24 May 1972)

A complete structural analysis of tin(II) iodide (SnI_2) has been carried out on the basis of three-dimensional X-ray diffraction data and refined to an R value of 0.049. The crystals are monoclinic, space group $C2/m$, with $a=14.17$, $b=4.535$, $c=10.87$ Å, and $\beta=92.0^\circ$. The compound is shown to possess a unique AX_2 layer structure in which the metal atoms occur in two distinct sites. Two-thirds of the tin atoms occupy sites similar to those in $SnCl_2$ ($PbCl_2$ type). The remaining tin atoms are in $PdCl_2$ -type chains which interlock with the $PbCl_2$ -type part of the structure to give almost perfect octahedral coordination. Significant Sn-I distances are all in the range 3.00–3.25 Å. Mössbauer spectroscopy fails to reveal the true complexity of the structure.

Introduction

Detailed studies on the preparation of tin(II) iodides (to be published elsewhere) afforded crystals of SnI_2 suitable for single-crystal X-ray diffraction. Structural

analysis was carried out as part of a wider programme to extend the data on the crystal chemistry of tin(II). Aylett (1969) suggested that SnI_2 and PbI_2 have the same structure (CdI_2 type), while Belotskii, Antipov, Nadochii & Dodik (1969) found that SnI_2 and PbI_2 form a continuous series of solid solutions of PbI_2 (CdI_2) structure, pure SnI_2 having a 'different structure'.

* Present address: Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185, U.S.A.

Experimental

Crystalline tin(II) iodide was prepared from tin metal (10 g) and iodine (14 g) heated under reflux in 2 M hydrochloric acid (90 ml). Further tin was added in approximately 0.5 g portions until the solution became very pale yellow and the freshly added tin retained its bright appearance for 10 min after addition, indicating that the solution was free from tin(IV). The solution was filtered rapidly into a conical flask warmed in a boiling water bath, and tin(II) iodide allowed to crystallize undisturbed as bath and flask cooled overnight to room temperature. To prevent oxidation to tin(IV), the tin(II) solution was maintained under an atmosphere of oxygen-free nitrogen, both under reflux and during cooling. The product was filtered off, washed with water containing a trace of hydrochloric acid, and dried *in vacuo* over potassium hydroxide and silica gel. Bulk analyses for stannous and total tin and iodide confirmed its identity and purity.

Crystal data

Tin(II) iodide (SnI_2) was obtained as brilliant red needles, elongated along [010]. The system is monoclinic, $a = 14.17 \pm 0.05$, $b = 4.535 \pm 0.016$, $c = 10.87 \pm 0.04$ Å, and $\beta = 92.0 \pm 0.2^\circ$. The unit-cell dimensions were refined using powder data (spacings for values of 2θ up to 60°) obtained on a Philips powder diffractometer type PW 1050/1 scanning at $2^\circ 2\theta$ per min with filtered Cu $K\alpha$ radiation and silicon as an internal standard (Table 1). Equi-inclination Weissenberg photographs for the layers $k=0, 1, 2$ and 3 were found to exhibit the systematic absences hkl absent for $h+k=2n+1$, and no others. Hence the space group is $C2$, Cm or $C2/m$. The formula weight ($\text{SnI}_2 = 372.52$) and six formula units per cell give an X-ray density of 5.34 g.cm^{-3} , compared with the measured value (displacement of benzene) of 5.29 g.cm^{-3} .

Intensity data

Intensity data for the layers $h, 0-3, l$ were obtained using a Hilger and Watts Y-190 linear diffractometer, with molybdenum radiation and a zirconia filter. Since SnI_2 was known to be susceptible to atmospheric oxidation, the crystal used for intensity measurement was encapsulated in Canada balsam. To minimize the exposure of the crystal to radiation (which accelerates its decomposition) the balanced filter facility of the diffractometer was not employed. Instead, four measurement cycles were made for each reflexion.

Net counts were extracted from the diffractometer data, using the program of North (1964), which applies an empirical absorption correction to the data for any given layer as a function of ω (the angle of rotation of the crystal at which the various reflexions occur). The correction factors are derived from the variation in the measured intensity of an axial reflexion (in this case 020) as the crystal is rotated.

Variation of intensity due to decomposition was

Table 1. Indexed powder diffraction pattern for tin(II) iodide (Maximum $2\theta = 60^\circ$.)

$d(\text{obs})$ (Å)	I/I_0	$d(\text{calc})$	Index
7.08	15	7.08	200
6.05	15	6.03	20 $\bar{1}$
5.83	40	5.84	201
4.395	20	4.384	20 $\bar{2}$
3.620	35	3.620	003
3.540	40	3.540	400
3.400	21	3.401	40 $\bar{1}$
3.370	22	3.360	112
3.330	40	3.332	401
3.274	100	3.270	20 $\bar{3}$
		3.268	310
3.170	88	3.179	203
3.090	40	3.109	311
3.023	22	3.014	40 $\bar{2}$
2.913	9	2.919	402
2.822	22	2.830	31 $\bar{2}$
2.745	24	2.759	113
2.714	11	2.715	004
2.585	10	2.576	40 $\bar{3}$
2.502	18	2.506	204
2.488	18	2.485	403
2.449	6	2.456	31 $\bar{3}$
2.356	7	2.359	51 $\bar{1}$
2.292	40	2.290	601
2.235	12	2.221	51 $\bar{2}$
2.199	70	2.193	60 $\bar{2}$
2.164	40	2.172	512
			005
2.159	30	2.157	220
2.137	28	2.137	602
2.102	14	2.111	221
		2.097	20 $\bar{5}$
2.054	5	2.057	205
2.032	6	2.029	51 $\bar{3}$
2.016	10	2.012	22 $\bar{2}$
1.967	16	1.974	513
1.943	4	1.946	603
1.927	6	1.932	115
		1.885	42 $\bar{1}$
1.888	6	1.881	40 $\bar{5}$
		1.844	223
1.846	11	1.844	223
1.824	10	1.823	405
			711
1.811	8	1.811	42 $\bar{2}$
			514
1.771	10	1.770	514
		1.773	800
1.762	10	1.766	71 $\bar{2}$
			206
1.740	10	1.739	024
			42 $\bar{3}$
1.704	5	1.700	80 $\bar{2}$
			71 $\bar{3}$
1.667	9	1.667	71 $\bar{3}$
		1.666	802
1.639	20	1.635	51 $\bar{5}$
			40 $\bar{6}$
1.601	4	1.600	31 $\bar{6}$
1.587	7	1.589	406
1.570	14	1.571	605
			025
1.565	10	1.568	316

monitored on a group of reference reflexions measured at the beginning, middle, and end of the data for each layer. Scale factors of 0.71, 0.8065, 1.0, and 1.10 for $k=0, 1, 2$ and 3 respectively were applied accordingly to correct for decomposition. It was found also that

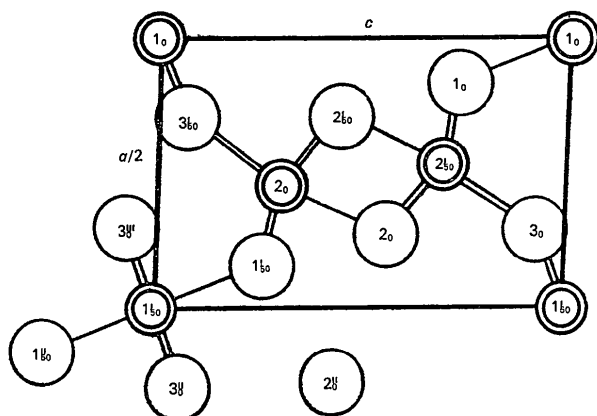


Fig. 1. Tin(II) iodide, projection on (010). Double and single circles are tin and iodine atoms respectively. Atom numbering is as in the text and Table 4. Subscript values are y coordinates in units of $b/100$. Single lines joining atoms represent tin-iodine contacts between atoms in the same layer perpendicular to b . Double lines indicate contacts between tin and iodine atoms in adjacent layers.

decomposition had destroyed the expected equivalence of some reflexions. Consequently, only reflexions with intensities at least three times the background count were accepted, and equivalent reflexions were averaged only if the counts agreed to within 20%; otherwise the larger intensity was accepted. In all, 234 independent intensities were obtained and converted to structure amplitudes in the usual way.

Computation

All calculations were carried out on an Elliott 803B computer. Intensity reduction, Fourier summation, and bond lengths and angles programs were made available by Daly, Stephens & Wheatley (1963). The block-diagonal least-squares program (PBRM 3/4) was lent by Dr Gareth Mair, formerly of the Royal Institution. For each atom refined this program uses a 3×3 matrix for positional parameters and either a 1×1 or 6×6 matrix for thermal parameters. A 2×2 matrix takes account of the interaction of scale and overall isotropic temperature factors. The weighting scheme used throughout this refinement was $w = 1/[1 - (KF_o - b)^2/a^2]$, where a and b had the values 120 and 200 respectively, on the same scale as KF_o . The errors associated with the positional parameters are expressed as variances and covariances, which are the appropriate elements of the inverse normal equations matrix (a_{ij}^{-1}) multiplied by $\sum w \Delta^2/(m - n)$, where m is the number of reflexions and n is the number of parameters refined (30 in the case of the refinement of SnI_2 in $C2/m$ with all the atoms given anisotropic temperature factors). In practice, the covariances were found to be negligible and the square roots of the variances are quoted as estimated standard deviations (e.s.d.). The anisotropic temperature factor is of the form $\exp[-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + klB_{23} + hlB_{13} + hkB_{12})]$.

Refinement of the structure

A first solution in the space group Cm was obtained from Patterson and Fourier methods, and refined by block-diagonal least-squares calculations to a final R value ($\sum |KF_o - F_c|/\sum |KF_o|$) of 0.102, as described by Moser & Trevena (1969). A major difficulty was the correct identification of the tin and iodine atoms. The selected arrangement was the only one to give sensible temperature factors. It further commended itself by giving sensible bond lengths and by revealing structural features common to some chemically related species. In short, it was the only one to make both crystallographic and chemical sense.

The almost centrosymmetric appearance of the preliminary structure as projected on (010) suggested an alternative refinement in the space group $C2/m$, which constrains the number of variable parameters. In $C2/m$, as in Cm , all atoms of the structure must lie on the mirror planes normal to the short axis b , because of space group considerations. The y coordinates are thus invariant. Similarly, the situation of all atoms on the mirror planes requires the vibration ellipsoids to have a principal axis parallel to $[010]$, and B_{12} and B_{23} to be zero and invariant. Adopting the higher symmetry reduces the number of unique atoms from three tin and six iodine atoms to two tin and three iodine atoms. Further, one of the tin atoms must now lie on a centre of symmetry, in order to meet the requirements of symmetry and cell contents.

Six cycles of block-diagonal least-squares refinement with isotropic temperature factors reduced the R value to 0.071. At this stage five reflexions were located which showed especially poor agreement. Errors in transcription from the manual data averaging process were corrected for these reflexions. A further ten cycles of refinement, with all the atoms refined anisotropically, reduced R to the final value of 0.049. Final shifts in the positional and vibrational parameters did not exceed 10^{-5} and 2×10^{-4} respectively. The final parameters are listed in Table 2, and observed and calculated structure factors in Table 3. A difference map calculated at this stage was virtually featureless.

Table 2. Final parameters for tin(II) iodide refined in $C2/m$

All unique atoms are placed on the mirror planes at $y=0$ and consequently their y coordinates and B_{12} and B_{23} of the anisotropic temperature factors are zero and invariant.

	Fractional coordinates*		Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)			
			B_{11}	B_{22}	B_{33}	B_{13}
Sn(1)	0.0000	0.0000	3.48	22.35	5.55	-1.68
Sn(2)	0.2662 (4)	0.3065 (4)	5.18	45.02	6.70	-2.15
I(1)	0.0780 (3)	0.7299 (3)	3.46	28.31	4.51	0.43
I(2)	0.3602 (3)	0.5609 (3)	2.87	33.25	3.37	-0.67
I(3)	0.3523 (3)	0.9239 (3)	3.60	39.78	5.54	-3.04

* Values in parentheses are estimated standard deviations in the last significant figure.

Table 3. Observed and calculated structure factors for tin(II) iodide in $C2/m$, scale $1.25 \times$ absoluteThe columns are h, k, l, F_o and F_c .

h	k	l	F_o	F_c
3	3	0	280	231
4	0	0	-129	-139
4	2	0	-299	-305
7	0	0	-159	-162
8	0	0	220	233
9	2	0	185	199
10	0	0	-109	-105
10	2	0	-142	-151
11	0	0	358	364
11	2	0	238	242
12	0	0	193	124
14	0	0	238	235
14	2	0	234	196
15	0	0	164	168
15	2	0	214	208
16	0	0	149	151
17	0	0	532	544
17	2	0	315	310
18	0	0	345	350
18	2	0	278	289
19	0	0	218	225
19	2	0	123	133
20	0	0	-94	-93
20	2	0	-84	-79
21	0	0	-99	-97
21	2	0	394	432
22	0	0	319	325
22	2	0	122	135
23	0	0	-271	-294
23	2	0	-215	-226
24	0	0	127	135
24	2	0	241	232
25	0	0	217	219
25	2	0	149	150
26	0	0	-128	-115
26	2	0	-378	-370
27	0	0	-156	-201
27	2	0	189	175
28	0	0	104	98
28	2	0	379	449
29	0	0	216	266
29	2	0	-149	-143
30	0	0	-123	-115
30	2	0	-234	-234
31	0	0	-178	-159
31	2	0	349	347
32	0	0	234	228
32	2	0	149	159
33	0	0	411	423
33	2	0	339	327
34	0	0	-21	20
34	2	0	446	440
35	0	0	232	270
35	2	0	215	219
36	0	0	139	173
36	2	0	143	142
37	0	0	446	470
37	2	0	148	173
38	0	0	-131	-159
38	2	0	134	149
39	0	0	311	319
39	2	0	230	223
40	0	0	491	491
40	2	0	268	258
41	0	0	-130	-118
41	2	0	-630	-612
42	0	0	-443	-438
42	2	0	564	577
43	0	0	463	432
43	2	0	-287	-282
44	0	0	314	305
44	2	0	249	252
45	0	0	229	226
45	2	0	188	174
46	0	0	-415	-410
46	2	0	-284	-251
47	0	0	296	298
5	3	-3	169	193
6	0	-3	-227	-223
6	2	-3	-234	-207
7	1	-3	139	137
7	3	-3	-139	-143
8	0	-3	439	430
8	2	-3	433	400
9	1	-3	332	343
9	3	-3	325	332
9	5	-3	-356	-362
10	0	-3	100	100
10	2	-3	292	293
11	1	-3	129	129
11	3	-3	136	143
12	0	-3	374	362
12	2	-3	195	189
13	1	-3	133	132
13	3	-3	194	194
14	0	-3	498	394
14	2	-3	230	241
15	1	-3	353	314
15	3	-3	250	246
16	1	-3	275	263
16	3	-3	167	161
17	0	-3	-144	-139
17	2	-3	-142	-156
18	0	-3	115	107
18	2	-3	-117	-111
19	0	-3	-133	-155
19	2	-3	-124	-115
20	1	-3	132	124
20	3	-3	-176	-170
21	0	-3	-143	-130
21	2	-3	-123	-97
22	0	-3	-132	-134
22	2	-3	133	134
23	0	-3	175	176
23	2	-3	145	143
24	0	-3	-130	122
24	2	-3	184	179
25	0	-3	170	157
25	2	-3	135	140
26	0	-3	-243	-250
26	2	-3	-189	-183
27	1	-3	348	353
27	3	-3	221	218
28	0	-3	-249	-272
28	2	-3	-176	-168
29	0	-3	355	369
29	2	-3	289	271
30	1	-3	185	179
30	3	-3	123	129
31	0	-3	-252	-246
31	2	-3	-145	-150
32	0	-3	292	283
32	2	-3	-220	-228
33	1	-3	-186	-167
33	3	-3	326	324
34	0	-3	481	376
34	2	-3	340	317
35	1	-3	151	147
35	3	-3	-184	-186
36	0	-3	-154	-144
36	2	-3	258	250
37	0	-3	226	200
37	2	-3	286	211
38	0	-3	157	138
38	2	-3	249	264
39	0	-3	241	219
39	2	-3	-190	-2
40	0	-3	-149	-148
40	2	-3	-137	-133
41	0	-3	-144	-125
41	2	-3	-944	-933
42	0	-3	-193	-182

below that containing the tin atom, giving $PdCl_2$ -type chains normal to (010). The octahedron is completed by two iodine atoms [I(1)] at 3.147 Å in the same layer as the tin atom. Infinite chains of edge-sharing octahedra thus extend normal to (010) (Fig. 2). Similar chains of rather more distorted edge-sharing octahedra are the main feature of the structures of anhydrous copper(II) chloride (Wells, 1947) and bromide (Helmholz, 1947);

(b) Sn(2) atoms, with their nearest neighbour iodine atoms, occur in pairs related by a twofold screw axis along [010] as shown in Figs. 1 and 3. Each Sn(2) is surrounded by seven iodine atoms. Six, in layers above and below that containing the tin atom, lie at the corners of a trigonal prism. The seventh and closest, in the same layer as the tin, belongs to the 2_1 -related prism

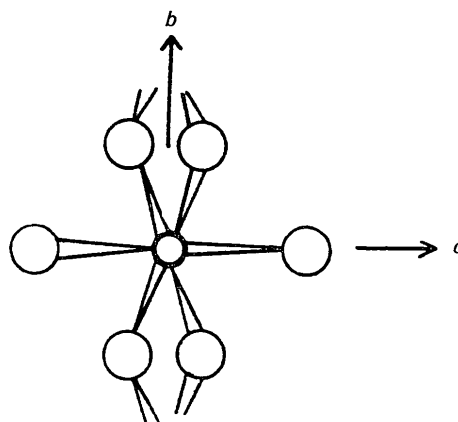


Fig. 2. Coordination of Sn(1), projection on (100). The smaller darker circle is the tin atom, and the larger circles iodine atoms.

The refinement in $C2/m$ is preferable to that in Cm because of both the lower R value and the more symmetrical coordination. However, a major assumption common to both of these solutions is the strict layering of the atoms, and hence the existence of the mirror planes. In order to determine the validity of this assumption, a further anisotropic refinement was attempted in the lower symmetry space group $C2$, but this produced no improvement in the degree of refinement of the structure. Accordingly, only the solution in the space group $C2/m$ is discussed further.

Description of the structure

Adoption of space group $C2/m$ confines all the atoms to layers at $y=0$ and $y=\frac{1}{2}$. In the (010) projection of half of the unit cell of tin(II) iodide two distinct tin environments are apparent (Fig. 1):

(a) Sn(1), lying on a centre of symmetry, is surrounded octahedrally by iodine atoms. Table 4(a) shows that there is no significant distortion of octahedral bond angles around this tin atom, and that differences in bond lengths are less than 1%. Four iodine atoms [I(3)] are 3.174 Å distant, in layers above and

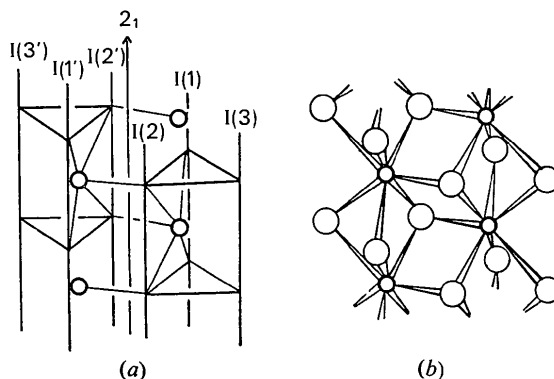


Fig. 3. The coordination of Sn(2), viewed along [100], with the positive direction of b tipped towards the observer through 20° . (a) Shows the trigonal prisms (outlined) associated with each of a pair of symmetry related Sn(2) atoms (small dark circles), and the relationship between them. Lines from the tin atoms indicate the positions of the five nearest neighbour iodine atoms. Iodine atom designations and the position of the twofold axis are given. (b) Shows the same set of atoms, joined by tin-iodine vectors, to demonstrate the coordination both of tin (smaller, darker circles) and of iodine (larger, lighter circles).

[Fig. 3(a)]. The prisms again extend infinitely normal to (010) and have iodine atoms I(1) and I(3) in common with the octahedron chains described above. The environment of Sn(2) closely resembles that found in other tin and lead dihalides which have the PbCl₂ layer structure (summary: Wyckoff, 1963).

Table 4. *Representative bond lengths and angles for SnI₂ (C2/m)*

Estimated standard deviations to the last significant digit are given in parentheses. Atom designations are as in Fig. 1.

(a) Coordination of Sn(1) (distorted octahedron)

Sn(1')—I(1')	3.147 (3) Å	I(1')—Sn(1')—I(3''')	89.4 (7)°
Sn(1')—I(3''')	3.174 (3)	I(1')—Sn(1')—I(3'')	90.6 (7)
I(1')—I(3'')	4.495 (4)	I(3'')—Sn(1')—*I(3'')	91.2 (6)
I(1')—I(3''')	4.445 (4)	I(3'')—Sn(1')—I(3''')	88.8 (6)
I(3'')—I(3''')	4.441 (4)		
I(3'')—*I(3'')	4.535 (16)		

(b) Coordination of Sn(2) (Trigonal prism with an additional iodine outside one prism face)

Sn(2')—I(1)	3.198 (5) Å	I(1)—Sn(2')—*I(1)	90.3 (9)°
Sn(2')—I(2)	3.251 (5)	I(1)—Sn(2')—I(2)	87.3 (7)
Sn(2')—I(3)	3.718 (5)	I(1)—Sn(2')—*I(2)	160.3 (9)
Sn(2')—I(2')	3.004 (5)	I(1)—Sn(2')—I(3)	77.5 (6)
I(1)—*I(1''')	4.535 (16)†	I(1)—Sn(2')—*I(3)	130.4 (7)
I(1)—I(2')	3.988 (4)	I(1)—Sn(2')—I(2')	80.0 (6)
I(1)—I(2)	4.451 (4)	I(2)—Sn(2')—*I(2)	88.5 (6)
I(1)—I(3)	4.348 (4)	I(2)—Sn(2')—I(3)	68.0 (4)
I(2')—I(2)	4.040 (4)	I(2)—Sn(2')—*I(3)	118.4 (5)
I(2')—I(3)	3.915 (4)	I(2)—Sn(2')—I(2')	80.4 (4)
I(3')—I(3''')	3.999 (4)	I(3)—Sn(2')—*I(3)	75.2 (2)
I(1')—I(2'')	4.193 (4)	I(3)—Sn(2')—I(2')	141.6 (3)
I(2'')—I(2'')	4.217 (4)		

* Indicates the atom is translated by **b**.

† This dimension appears three times in all, once for each prism edge parallel to **b**.

Discussion

Both the tin sites in tin(II) iodide can be compared with sites in previously determined structures of other tin(II) compounds.

(a) Octahedral site [Sn(1)]

Octahedral coordination of tin(II) occurs in the cubic metalloid SnTe, which has the NaCl structure (*a*'=6.313 Å; summary: Wyckoff, 1963) and in the cubic caesium trihalogenostannates(II) thought to have a perovskite structure (Barrett, Bird, Donaldson & Silver, 1971).

At first sight, such coordination appears to offer a way of calculating a radius for truly ionic Sn²⁺. Indeed, the radii calculated from SnI₂ (0.92–0.93 Å), SnTe (0.925 Å) and cubic CsSnBr₃ (0.95 Å) are in remarkable agreement with each other and with the 0.93 Å predicted by Ahrens (1952) for ionic six-coordinate tin(II).

However, SnTe is clearly not a purely ionic compound, and the Sn–Te bond length of 3.16 Å can be interpreted almost as well in terms of atomic radii (say Sn 1.62 + Te 1.60 = 3.22 Å) as in terms of ionic radii (Te²⁻ in contact 2.23 + Sn²⁺ 0.93 = 3.16 Å). In other

words, the bond length sheds little, if any, light on the relative preponderance of metallic or ionic bond character.

In the case of SnI₂, the average Sn–I bond length in the octahedra is 3.165 Å. Of the I···I distances (octahedron edge), the longest is that of the layer spacing (*b*=4.535 Å) and the shortest that of the shared edge of the octahedra (4.441 Å).

Assuming the iodine atoms to be in contact gives an iodine radius of about 2.24 Å, a value in broad agreement with, if slightly larger than, the 2.16 Å commonly quoted for I⁻, or the 2.20 Å recently suggested for I⁻ by Shannon & Prewitt (1968). This assumption of iodide ions in contact certainly appears to be the most sensible way of accounting for the layer spacing of 4.53 Å, but the I···I distance expected for pure van der Waals contact (4.3 Å, Wells, 1962) is sufficiently close that alternative interpretations cannot be ruled out. Appreciable covalent bonding at the octahedral site can probably be ruled out, as this should result in much shorter Sn–I bonds (2.73 Å in gaseous SnI₂, Lister & Sutton, 1941) than the 3.15 Å minimum found at this site.

(b) Trigonal prism site [Sn(2)]

This type of site is found in tin(II) halides with the PbCl₂ structure, *e.g.* in SnCl₂ (van den Berg, 1961) and SnBr₂ and SnClI currently under investigation in this laboratory. More detailed examination of bond lengths in each case shows that one edge of the prism [in the present case I(3)] is sufficiently distant from the enclosed metal atom to warrant its exclusion from the primary coordination of the metal atom.

In each case, the tin atom has three nearest neighbour halogen atoms [here I(1) in adjacent layers and I(2') in the same layer as Sn(2')], all lying to one side of the tin in a trigonal pyramidal grouping with tin at the apex. The trigonal pyramids share two corners to form chains parallel to the shortest unit cell edge, *i.e.* normal to the layers. In all cases there are also two next nearest neighbours [here I(2) in layers adjacent to Sn(2')] which link the chains of pyramids in pairs (Fig. 3). The tin(II) atoms can thus be regarded as primarily five-coordinate with all the halogen atoms lying to one side of them.

In the present structure, all five Sn–I bonds fall within the range 3.00–3.25 Å. Inclusion of the secondary coordination [Sn(2') to I(3)] makes the tin seven-coordinate, but the bonds involved (3.72 Å) are clearly of a different order. The shortest Sn–I bond [Sn(2')–I(2'), 3.00 Å] is appreciably shorter than any other Sn–I bond in the entire structure, and can be construed to have appreciable covalent character.

The coordination of iodine by tin provides a more coherent view of the two tin environments. Iodine atoms I(1) and I(2) each have three nearest neighbour tin atoms. I(3) has two or four nearest neighbour tin atoms, depending on whether coordination to Sn(2') is included, *i.e.* depending on whether Sn(2') is regarded

as five- or seven-coordinate. I(1) [and I(1')] are common both to the octahedral chain coordination of Sn(1)-type tin atoms and to the double chain of Sn(2)-type (5-coordinate) tin atoms. These two chains, both parallel to [010], can be regarded as forming a continuous puckered sheet parallel to (201). All Sn-I bonds within this sheet are in the range 3.00–3.25 Å. The longer (3.72 Å) bonds, *e.g.* Sn(2')–I(3), can then be thought of as connecting the (201) sheets in a three-dimensional structure.

Tin(II) iodide thus has a layer structure in a dual sense: crystallographically in terms of (010) layering, and in a crystal-chemical sense in terms of puckered (201) sheets of most tightly bonded atoms. The latter view of the structure is confirmed by an analysis of the Pauling electrostatic bond strengths. Sn–I bond strengths within the puckered (201) sheets are uniformly $\frac{1}{3}$, whereas the longer sheet-connecting Sn(2)–I(3) bonds are of bond strength $\frac{1}{5}$.

Attempts were made to elucidate the nature of the bonding in SnI₂ by other experimental approaches.

Solid solutions with PbI₂

Tin(II) iodide was crystallized from solutions containing lead(II), in the hope that lead(II) might selectively replace tin(II) in either the octahedral or the prism site of SnI₂. X-ray powder diffraction and chemical analysis of the phases obtained revealed that compounds of the type Sn_xPb_(1-x)I₂ were produced, with *x* in the range of 0.0–0.5. All had the PbI₂ (cadmium iodide) structure, confirming in part the results of Belotskii (1969). In the presence of high concentrations of tin(II), crystals with the morphology of tin(II) iodide were obtained along with the hexagonal plates of the CdI₂ type, but it was not possible to determine with certainty whether the crystals contained lead.

Mössbauer spectroscopy

The most complicated Sn^{119m} Mössbauer spectrum arising from the proposed X-ray structure would consist of four lines, corresponding to two quadrupole split absorptions, one for each tin site. The relative area of the pairs should be two to one in favour of Sn(2), although differences in recoil-free fractions for the two sites might cause departures from the ideal ratio. Simpler cases would arise when one or both of the tin sites gives a single line absorption, but the relative area condition should still apply.

The Mössbauer spectrum of tin(II) iodide at 80°K was obtained with a barium stannate source at room temperature. β-Sn, also at room temperature, provided the tin reference absorber. The resulting spectrum appeared at first sight to consist of a single line, but an improved fit was obtained on a two-line model. The final parameters produced lines of almost identical area and line-width (full-width at half height) of 0.99 and 1.00 mm.sec⁻¹. The isomer shifts of the lines

relative to β-Sn at room temperature are 1.65 and 1.27 ± 0.01 mm.sec⁻¹. If they are regarded as components of a quadrupole split absorption these values correspond to an isomer shift of 1.46 ± 0.01 mm.sec⁻¹ relative to β-Sn and a quadrupole splitting of 0.37 ± 0.02 mm.sec⁻¹. On this interpretation, the values are in agreement with previously published data *e.g.* those of Donaldson (1967), making allowance for the different reference points used in the calculation of isomer shifts.

Interpretation of the spectrum is, however, far from straightforward. If the lines are indeed components of a quadrupole split absorption, then the two tin sites in the structure must have very similar Mössbauer parameters so that they are not observed separately. If the lines are attributed one to each tin site, then the relative areas are not those expected from the structure. (A similar discrepancy between Mössbauer data and structural requirements has been reported for Sn₃BrF₅ by Donaldson, 1969.)

The only firm conclusion to be drawn at this stage is that even the octahedral Sn(1) cannot be purely ionic. The isomer shift of the 5s²Sn²⁺ ion has been estimated as about +5.0 mm.sec⁻¹ relative to β-Sn (Donaldson, 1967) compared with the highest value of +1.65 mm.sec⁻¹ in the present spectrum. The relatively low Mössbauer shifts could be accounted for if some of the 5s electrons of the octahedral Sn(1) atoms were involved in conduction bands.

Similar low Mössbauer isomer shifts were found by Barrett *et al.* (1971) for the cubic CsSnX₃ phases (*e.g.* +1.33 mm.sec⁻¹ relative to β-tin for CsSnBr₃) and similar explanations suggested.

Further work on the relationship of the Mössbauer spectrum of tin(II) iodide to colour and conductivity at different temperatures is now in progress, and should throw further light on the bonding problems posed by this structure.

Conclusion

The X-ray structure of tin(II) iodide shows that the compound has a layer structure closely related to the lead(II) chloride type, two-thirds of the tin cations occupying sites with coordination characteristic of this type of structure. However, restrictions on anion packing result in the remaining tin atoms being coordinated in octahedral sites closely resembling those of tin(II) in tin telluride. It has not proved possible to confirm the X-ray structure in detail by Mössbauer spectroscopy.

We are indebted to Mrs Lorna Ingram for the X-ray intensity data, and to Dr F. W. D. Woodhams of the Department of Natural Philosophy of this University and Dr W. Parker of the Physics Department of Exeter University for obtaining and interpreting the Mössbauer data. One of us (I.C.T.) is grateful to the Tin Research Council for a maintenance grant.

References

- AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, **2**, 155.
 AYLETT, B. J. (1969). *Prog. Stereochem.* **4**, 231.
 BARRETT, J., BIRD, S. R. A., DONALDSON, J. D. & SILVER, J. (1971). *J. Chem. Soc. (A)*, p. 3105.
 BELOTSKII, D. P., ANTIPOV, I. N., NADTOCHIL, V. F. & DODIK, S. M. (1969). *Inorg. Mater.* **5**, 1583.
 BERG, J. M. VAN DEN (1961). *Acta Cryst.* **14**, 1002.
 DALY, J. J., STEPHENS, F. S. & WHEATLEY, P. J. (1963). Monsanto Research S. A., Final Report No. 52.
 DONALDSON, J. D. (1967). *Prog. Inorg. Chem.* **8**, 287.
 DONALDSON, J. D. (1969). *J. Chem. Soc. (A)*, p. 2358.
 HELMHOLZ, L. (1947). *J. Amer. Chem. Soc.* **69**, 886.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
 LISTER, M. W. & SUTTON, L. E. (1941). *Trans. Faraday Soc.* **37**, 406.
 MOSER, W. & TREVENA, I. C. (1969). *Chem. Commun.* p. 25.
 NORTH, A. C. T. (1964). *J. Sci. Instrum.* **41**, 42.
 SHANNON, R. D. & PREWITT, C. T. (1968). *Acta Cryst.* **25**, 925.
 WELLS, A. F. (1947). *J. Chem. Soc.* p. 1670.
 WELLS, A. F. (1962). *Structural Inorganic Chemistry*. 3rd Ed., p. 316. Oxford: Clarendon Press.
 WYCKOFF, R. W. G. (1963). *Crystal Structures*. 2nd Ed. Vol. I, pp. 90, 198, 299, 403. New York, London and Sydney: Interscience.

Acta Cryst. (1972). **B28**, 2971

The Crystal Structure of 6-Methyluracil-5-acetic Acid*

BY RICCARDO DESTRO† AND RICHARD E. MARSH

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, U.S.A.

(Received 24 May 1972)

Crystals of 6-methyluracil-5-acetic acid are monoclinic, space group $P2_1/n$, with $a=4.8929$ (1), $b=12.6368$ (3), $c=12.7455$ (1) Å, $\beta=99.174$ (2)°, $Z=4$. Approximately 1600 intensity data for two different crystals were collected on an automated diffractometer; one crystal was an approximate cube 0.16 mm on an edge and the second was a sphere 0.18 mm in diameter. The structure was derived by direct phasing methods and refined by full-matrix least-squares analysis. The two data sets were treated separately, and both led to the same parameters (within three e.s.d.'s) except for the coefficient of secondary extinction, which was 25% (four e.s.d.'s) smaller for the crystal that had been ground to a sphere. Final refinement, which included anisotropic temperature coefficients for all atoms including hydrogen, led to an R index of 0.036 and standard deviations of about 0.0015 Å in the positions of the heavy atoms. The pyrimidine ring is slightly nonplanar, being folded along the C(2)···C(5) axis to relieve strain between the exocyclic substituents. The structure features an off-set stacking of parallel pyrimidine rings at a separation of about 3.29 Å, and hydrogen bonding across centers of symmetry to form base-pairs.

Introduction

Our crystal structure investigation of 6-methyluracil-5-acetic acid, $C_7H_8N_2O_4$, was begun in 1967. Originally inspired by our continuing interest in the geometry and packing of nucleic acid derivatives, it served as an early test in our Laboratories of the power of direct methods of phase determination and of the accuracy of diffractometer measurements. At the beginning of the analysis, the author who carried out all of the experimentation (RD) knew nothing as to the nature of the compound other than that it contained

no atom heavier than oxygen; it is a testimonial to the power of present-day methods that RD knew the complete make-up of the molecule – including the identities of the various atom types and the locations of the protons – within two weeks after completing the data collection.

Experimental

Crystals in the form of colorless needles, elongated along a , were obtained from Professor James English of Yale University as part of the Treat B. Johnson collection. Unit-cell dimensions were obtained from a least-squares treatment of 84 measurements on zero-level Weissenberg photographs about the a and b axes, taken at 20 (1)°C; the films were held in the asymmetric position, following the Straumanis technique. The space group $P2_1/n$ was indicated by the absence of reflections $h0l$ with $(h+l)$ odd and $0k0$ with k odd. The density was measured by flotation in an aqueous

* Contribution No. 4463 from the Arthur Amos Noyes Laboratory of Chemical Physics. This investigation was supported in part by Public Health Service Research Grant No. GM 16966, from the National Institute of General Medical Sciences.

† Present address: Istituto di Chimica Fisica, Università di Milano, Via C. Saldini 50, 20133 Milano, Italy.