Acta Cryst. (1958). **11**, 41

The Crystal Structure of Zinc Salicylate Dihydrate*

By Harold P. Klug, Leroy E. Alexander and G. Gardner Sumner

Department of Chemical Physics, Mellon Institute, Pittsburgh 13, *Pa., U.S.A.*

(*Received* 13 *May* 1957)

The crystal structure of zinc salicylate dihydrate has been determined by two-dimensional Fourier methods. The molecule, $Zn(C_7H_5O_3)_2.2\,H_2O$, possesses a twofold axis, and exists as a unit in the structure. Except for two oxygen atoms, the entire salicylate radical is planar. Oxygen coordination about the zinc is tetrahedral. The water molecules play a dominant role in the framework structure. Their oxygen atoms are a part of the primary coordination sphere around the zinc atoms, and through hydrogen bonds they hold the crystal together in the *a* and *b* directions. Binding forces in the *c* direction are van der Waals in character.

Introduction

Because of the wide use of the salicylates biologically, both as medicinal agents and as antiseptics, a study of several anhydrous and hydrated salicylates was initiated to learn more about the salicylate radical and its environment in these important compounds. The presence of the *o*-hydroxyl group, and of water molecules in the hydrates, suggested the possibility of considerable hydrogen bonding, which would prove of special interest to structural chemists. Prior to this investigation zinc salicylate dihydrate has been described as a trihydrate, and it is not clear why an earlier X-ray crystallographic study (Clark & Kao, 1948) failed to disclose this error. Clark & Kao did report the monoclinic symmetry of the crystal and the following lattice constants: $a = 15{\cdot}40 \pm 0{\cdot}02$, $b = 5{\cdot}37 \pm 0{\cdot}01$, $c = 9{\cdot}18 \pm 0{\cdot}01$ Å, $\beta = 93{\cdot}8° \pm 0{\cdot}2°$. Their study further reported a measured density of 1·64 g.cm.$^{-3}$ and two molecules of the trihydrate per unit cell. The ideal density calculated from these data, and based on a trihydrate, is 1·73 g.cm.$^{-3}$, not 1·653 g.cm.$^{-3}$ as listed. Extinctions characteristic of space groups *C*2/*m*, *C*2, or *Cm* were found, but no further study of the structure was attempted.

Experimental

Zinc salicylate dihydrate, $Zn(C_7H_5O_3)_2.2\,H_2O$, was prepared by mixing equal volumes of 2-molar sodium salicylate and 1-molar zinc chloride solutions at room temperature (Clark & Kao). The fine crystalline precipitate of the dihydrate, which separated after a few seconds, was filtered off by vacuum, washed with water, and dried. Hot saturated aqueous solutions of this crystalline powder, on slow cooling in a Dewar vessel, yielded fine tabular or prismatic single crystals suitable for X-ray study. Early in the crystallization a mass of long fine needle-like crystals may appear, which disappear again on standing in the mother liquor. No attempt was made to investigate these needle crystals. Analytical confirmation of the water content was attempted through analysis for zinc*, rather than through loss of water, lest the heating result in some decomposition of the salicylate radical. Calculated per cent zinc for trihydrate, 16·6; for dihydrate, 17·3; found: 16·79, 16·78. Since the X-ray analysis demonstrates conclusively that the compound is a dihydrate, the excess water over 2 molecules per molecule of zinc salicylate (about $\frac{3}{4}$ molecule) is considered to be of an adsorbed nature or present in inclusions.

Minute prismatic crystals were chosen for X-ray study in order to minimize the effects of absorption. From zero-, first-, and second-level b^*c^* precession photographs, zero- and first-level a^*b^* precession photographs, and zero-level a^*c^* Weissenberg photographs, prepared with Cu $K\alpha$ radiation, the space-group absences and the lattice constants were obtained. The observed extinction, (hkl) with $h+k = 2n+1$, is characteristic of space groups *C*2/*m*, *C*2, and *Cm*. Piezoelectric tests† on the crystals indicated definite piezoelectric activity, with resonances between 0·5 and 1·5 megacycles per sec. The crystals thus have no center of symmetry, and space group *C*2/*m* is eliminated from further consideration. The short *b* axis and the appearance of the $(h0l)$ and $(hk0)$ projections further eliminate *Cm*, and fix *C*2 as the correct space group. The lattice constants from this study are:

$$a = 15{\cdot}43 \pm 0{\cdot}02, \quad b = 5{\cdot}35 \pm 0{\cdot}02, \quad c = 9{\cdot}18 \pm 0{\cdot}02 \text{ Å}, \quad \beta = 93{\cdot}8° .$$

Two molecules of the dihydrate are present in the unit

---

* Preliminary results of this study were reported at the summer meeting of the American Crystallographic Association, Pasadena, California, 30 June 1955.

* Analyses by the Department of Analytical Chemistry, Mellon Institute.

† The kindness of Dr Ray Pepinsky of Pennsylvania State University in making these tests is gratefully acknowledged.

cell, and the ideal density on this basis is 1·65 g.cm.$^{-3}$, in good agreement with the measured density 1·64 g.cm.$^{-3}$ (Clark & Kao, 1948).

Complete intensity data for the ($h0l$) and ($hk0$) zones were obtained from Cu $K\alpha$ Weissenberg photographs in conjunction with the multiple-film technique. The ($h0l$) data comprise 172 different reflections out of a total of 178 that are accessible, and the ($hk0$) data represent all 59 forms available. All intensities were estimated visually, using a graded intensity scale. After applying the appropriate Lorentz and polarization correction (Buerger & Klein, 1945), the intensities were reduced to relative F_o values.

Determination of atomic positions

The determination of the structure was approached from the centrosymmetric ($h0l$) projection of space group $C2$. It is seen that the two zinc atoms per cell can be assigned positions at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0 (with their y parameter assumed to be zero), and that their contribution to all F's will be positive. Then, with all F_{h0l} given a positive sign, the ($h0l$) electron-density projection was prepared. The four salicylate radicals and oxygen atoms of four water molecules were very clearly discernible on the projection. The benzene ring of the salicylate radical, however, was considerably distorted from a regular hexagon, indicating a large angle of tilt relative to the plane of the projection. Preliminary parameters from this projection gave F_c's which indicated only 10 incorrect signs. Four electron-density projections (Fig. 1) and four difference syntheses ($F_o - F_c$) served to refine the x and z parameters (Table 1). The complete absence on this projection of spurious peaks, which would have been present in this centrosymmetrical treatment had the space group been Cm, again ruled out Cm and its further consideration.

Throughout the structure-factor calculations McWeeny (1951) scattering factors for carbon and oxygen were used. For zinc the average of the Thomas–Fermi (*Internationale Tabellen*) and the Pauling–Sherman scattering factors was used, as suggested by Pauling & Sherman (1932). Corrections were applied to the f_{Zn} values for the dispersion of the K electrons (James, 1954). It was necessary to introduce an anisotropic temperature factor for each kind of atom. The expression used was that of Hughes (1941) and Hughes & Lipscomb (1946):

$$f_{\mathrm{Zn}} = f_{o\mathrm{Zn}} \exp\left[-(B_1+B_3\cos^2\varphi)(\sin\theta/\lambda)^2\right].$$

Here B_1 is the constant in the direction of minimum vibration (normal to the (100) planes), B_1+B_3 is the constant in the direction of maximum vibration (normal to the (001) planes), and φ is the angle between the normal to the reflecting plane and the direction of maximum vibration. Best values for these constants are listed in Table 2. The scale factor for bringing F_o into agreement with F_c for the ($h0l$) zone was 8·66. Final calculated ($h0l$) structure factors are listed in Table 3. Excluding (001) and (201), whose F_o values

Table 1. *Atomic parameters*

Atom	x	y	z
Zn	0·000	0·000	0·000
C_1	0·432	0·813	0·176
C_2	0·377	0·997	0·245
C_3	0·287	0·019	0·208
C_4	0·236	0·198	0·272
C_5	0·273	0·348	0·375
C_6	0·361	0·320	0·409
C_7	0·412	0·150	0·349
O_1	0·514	0·822	0·202
O_2	0·399	0·680	0·086
O_3	0·250	0·848	0·109
$O_4(H_2O)$	0·075	0·730	0·111

Table 2. *Temperature-factor constants*

Atom	B_1 (Å^2)	B_2 (Å^2)	B_3 (Å^2)
Zn	1·35	1·00	2·65
C	1·35	1·60	2·65
O	2·00	1·00	2·65

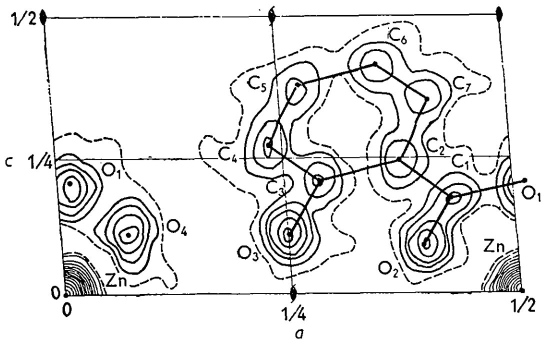

Fig. 1. Electron-density projection of the asymmetric unit of zinc salicylate dihydrate on (010). Contours are at intervals of 1 e.Å^{-2} except for the zinc contours, which are at 2 e.Å^{-2} intervals. The 1-electron contour is shown as a broken line.

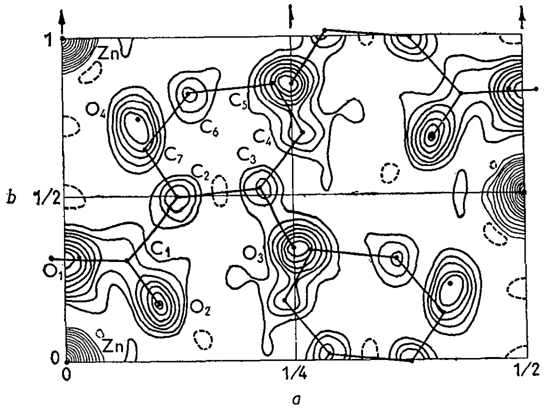

Fig. 2. A portion of the ($hk0$) electron-density projection of zinc salicylate dihydrate. Contours are at intervals of 1 e.Å^{-2} except for the zinc contours, which are at 2 e.Å^{-2} intervals. The 1-electron contour has been omitted for greater clarity. The zero-electron contour is shown as a broken line.

Table 3. *Observed and calculated structure factors*

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
200	35	38	202	26	23	204	34	30	206	53	51	20$\bar{8}$	9	5	020	40	37
400	59	$\underline{64}$	402	0	3	404	48	49	406	29	26	40$\bar{8}$	12	10	220	24	20
600	39	44	602	32	26	604	53	52	606	34	$\underline{33}$	60$\bar{8}$	0	3	420	44	51
800	70	71	802	16	15	804	32	33	806	18	18	80$\bar{8}$	0	4	620	50	65
1000	35	33	1002	24	19	1004	29	27	1006	15	17	100$\bar{8}$	8	7	820	32	42
1200	46	42	1202	33	26	1204	17	23	1206	0	1	120$\bar{8}$	12	12	1020	35	36
1400	25	30	1402	0	0	1404	21	18	1406	13	17	140$\bar{8}$	6	8	1220	9	12
1600	18	18	1602	0	1	1604	10	12							1420	24	17
1800	11	7	1802	0	3	1804	12	11	20$\bar{6}$	27	21	209	0	9	1620	21	15
									40$\bar{6}$	36	31	409	10	9	1820	19	17
001	76	$\underline{102}$	20$\bar{2}$	64	68	20$\bar{4}$	44	41	60$\bar{6}$	16	19	609	8	6			
002	18	16	40$\bar{2}$	26	19	40$\bar{4}$	26	24	80$\bar{6}$	19	19	809	10	8	130	36	37
003	7	$\underline{7}$	60$\bar{2}$	41	42	60$\bar{4}$	74	78	100$\bar{6}$	19	19	1009	10	11	330	66	70
004	8	7	80$\bar{2}$	36	27	80$\bar{4}$	32	29	120$\bar{6}$	27	31				530	41	31
005	35	27	100$\bar{2}$	27	22	100$\bar{4}$	25	$\underline{25}$	140$\bar{6}$	15	13	20$\bar{9}$	12	13	730	32	25
006	0	1	120$\bar{2}$	22	27	120$\bar{4}$	20	24	160$\bar{6}$	9	7	40$\bar{9}$	9	7	930	7	11
007	0	2	140$\bar{2}$	20	21	140$\bar{4}$	9	3				60$\bar{9}$	12	6	1130	36	39
008	20	18	160$\bar{2}$	18	22	160$\bar{4}$	15	18	207	12	9	80$\bar{9}$	8	6	1330	24	20
009	15	16	180$\bar{2}$	13	14	180$\bar{4}$	17	21	407	21	22	100$\bar{9}$	7	9	1530	23	20
0010	11	13							607	29	27				1730	12	6
0011	10	9	203	34	26	205	46	44	807	9	$\underline{7}$	2010	0	4			
			403	19	11	405	33	31	1007	12	15	4010	0	6	040	23	23
201	97	138	603	30	23	605	39	39	1207	0	4	6010	6	4	240	29	27
401	53	$\underline{52}$	803	37	30	805	23	27	1407	7	8				440	21	19
601	21	20	1003	37	39	1005	25	25				20$\overline{10}$	8	8	640	25	25
801	9	3	1203	23	22	1205	0	6	20$\bar{7}$	21	13	40$\overline{10}$	15	15	840	10	11
1001	40	38	1403	21	$\underline{25}$	1405	13	16	40$\bar{7}$	10	5	60$\overline{10}$	10	8	1040	22	21
1201	37	31	1603	0	2	1605	4	9	60$\bar{7}$	9	7				1240	8	3
1401	0	1	1803	5	8				80$\bar{7}$	19	18	2011	0	0	1440	23	19
1601	16	23				20$\bar{5}$	37	34	100$\bar{7}$	12	13				1640	13	13
1801	0	5	20$\bar{3}$	7	6	40$\bar{5}$	40	31	120$\bar{7}$	19	16	20$\overline{11}$	10	8			
			40$\bar{3}$	30	25	60$\bar{5}$	73	74	140$\bar{7}$	7	6	40$\overline{11}$	11	$\underline{13}$	150	17	10
20$\bar{1}$	18	8	60$\bar{3}$	39	38	80$\bar{5}$	14	15	160$\bar{7}$	11	12	60$\overline{11}$	9	4	350	22	11
40$\bar{1}$	59	66	80$\bar{3}$	38	33	100$\bar{5}$	20	$\underline{18}$							550	14	11
60$\bar{1}$	32	26	100$\bar{3}$	16	8	120$\bar{5}$	0	7	208	0	1	110	32	19	750	14	15
80$\bar{1}$	58	61	120$\bar{3}$	14	$\underline{13}$	140$\bar{5}$	34	40	408	12	14	310	43	53	950	8	13
100$\bar{1}$	32	31	140$\bar{3}$	0	7	160$\bar{5}$	7	6	608	0	3	510	36	43	1150	8	9
120$\bar{1}$	43	44	160$\bar{3}$	12	10	180$\bar{5}$	14	15	808	26	25	710	36	43	1350	13	10
140$\bar{1}$	27	23	180$\bar{3}$	15	12				1008	0	2	910	39	30			
160$\bar{1}$	20	21							1208	0	4	1110	37	23	060	25	29
180$\bar{1}$	17	20										1310	32	24	260	11	10
												1510	10	10	460	12	12
												1710	18	19	660	6	7
												1910	13	10	860	19	17

are evidently affected by extinction, the reliability index, $R(h0l)$, is 0·145.

Rough estimates of the tilt of the salicylate radical from the $(h0l)$ projection served for the prediction of preliminary y parameters. A few such trials permitted the calculation of phase angles for the $(hk0)$ reflections and gave R values around 0·30. The $(hk0)$ projections were readily interpreted except for one spurious peak. There had been no evidence on the $(h0l)$ projection (Fig. 1) for the presence of the third water molecule of a trihydrate, and attempts to interpret this $(hk0)$ peak as such were entirely unsuccessful. It was finally discovered that an incorrect parameter was being used for one oxygen atom. On correcting this parameter the spurious peak disappeared (Fig. 2). The y parameters steadily refined to the values of Table 1, and the final $(hk0)$ calculated structure factors (Table 3) have an R value of 0·163. Anisotropic temperature factors, B_1 and B_1+B_2, for the various kinds of atoms were likewise required in this zone, the values of B_2 being listed in Table 2. The scale factor for the $(hk0)$ data is 5·20.

Description of the structure

1. *The framework*

Fig. 3 shows a projection of the structure on (010). The discrete salicylate radicals and the coordination around the zinc atoms are the most evident features of the structure. The water molecules, O_4, and the salicylate radicals are linked to form double layers in the ab plane, partly through the Zn–O bonds of the zinc coordination polyhedra, and partly through a series of hydrogen bonds formed by the water molecules. Two water molecules, O_4, are associated with each zinc coordination sphere, and with two salicylate radicals make up the molecule of zinc salicylate dihydrate, $Zn(C_7H_5O_3)_2 . 2\,H_2O$, which can be seen as a unit in the structure. Each molecule of the dihydrate, accordingly, possesses a twofold axis of symmetry. The three different hydrogen bonds in the structure have been indicated in Fig. 3(a) by broken lines. The distance O_3–O_2 is the strong internal hydrogen bond of the salicylate radical formed between the o-hydroxyl group and the carbonyl oxygen of the carboxyl group (Cochran, 1953). A second strong hydrogen bond, the distance O_4–O_1, is actually a bond between successive zinc polyhedra in the b direction (Fig. 3(b)). Weaker hydrogen bonds, O_4–O_3, hold the layers together in the a direction. The forces in the c direction between neighboring double layers are only van der Waals in character, the closest C–C approaches being 3·63 and 3·75 Å.

The bc projection, Fig. 3(b), depicts the strong tilt of the salicylate radical relative to the b and c axes, and makes very evident the polar nature of the twofold axes. Successive Zn–O coordination groups of the molecules are tied together along the b axis by the strong hydrogen bond, O_4–O_1, of length 2·55 Å. Other distances indicated on Fig. 3(b) are the same C–C inter-

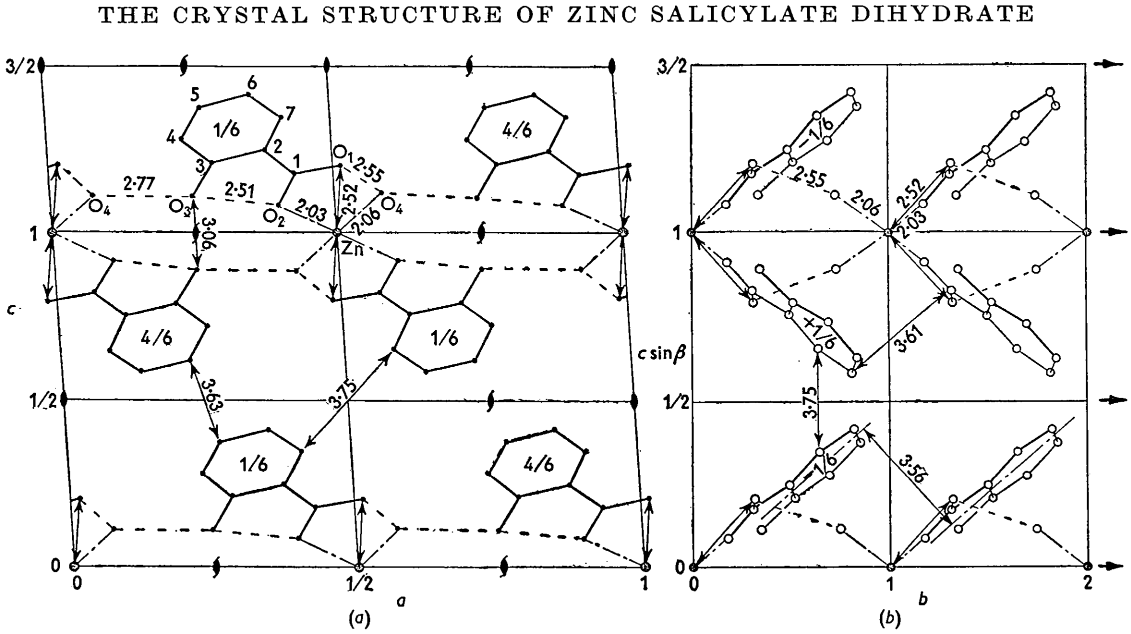

Fig. 3. (a) A diagram of the structure as projected on (010). Broken lines represent hydrogen bonds, and chain lines the Zn–O bonds. Fractions on the benzene rings indicate their distances along b from the origin. (b) Projection of part of the structure along the a axis. For clarity those molecules with zinc atoms at b = 0·5 have been omitted. These would superpose an identical pattern with a translation half way along b. The hydrogen bonds and Zn–O bonds are represented as in (a), and the fractions are benzene ring distances along the a axis.

layer distance, 3·75 Å, of Fig. 3(a), the C_1–C_6 distance of 3·61 Å between neighboring molecules along b, and the perpendicular distance, 3·56 Å, between planes of successive salicylate radicals.

The water molecules are seen to play a dominant role in the framework structure. Their oxygen atoms are a part of the primary coordination sphere around the zinc ions, and through hydrogen bonding they hold the structure together in the a and b directions. A pronounced cleavage observed while trying to grind tiny crystal spheres of the material is in line with the weak bonds in the c direction.

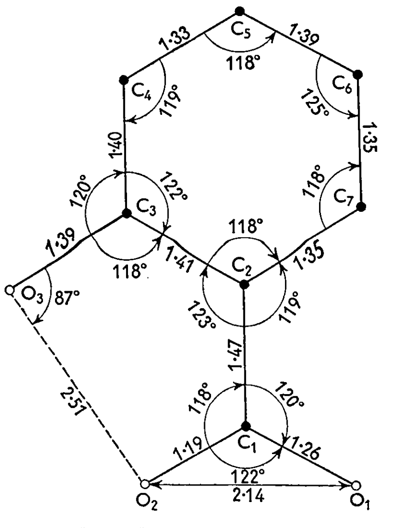

Fig. 4. Measured bond lengths and bond angles of the salicylate radical.

2. *The salicylate radical*

Final dimensions and bond angles of the salicylate radical are presented in Fig. 4. Because of the swamping effect of the zinc atoms, refinement beyond that here reported was not practicable. Accordingly, the probable error for the bond distances is estimated at ±0·03 Å and for the bond angles at not more than ±2°. These limitations make elaborate interatomic distance considerations of possible resonance structures for the radical unprofitable. A brief comparison of distances with those previously reported is of interest, however. Table 4 lists the results of this study together with

Table 4. *Interatomic distances in salicylic acid,* H*A*, *and the salicylate radical,* A^-

Bond	A^- (This study)	HA (Cochran)	HA (D. & S.)	A^- (D. & S.)
C_1–C_2	1·47 Å	1·458 Å	1·42 Å	1·48 Å
C_2–C_3	1·41	1·393	1·37	1·38
C_3–C_4	1·40	1·411	1·40	1·38
C_4–C_5	1·33	1·369	1·38	1·35
C_5–C_6	1·39	1·374	1·37	1·39
C_6–C_7	1·35	1·371	1·39	1·38
C_7–C_2	1·35	1·414	1·40	1·41
C_1–O_1	1·26	1·333	1·34	1·29
C_1–O_2	1·19	1·241	1·29	1·27
C_3–O_3	1·39	1·361	1·33	1·37
O_1–O_2	2·14	—	2·22	2·27
O_2–O_3	2·51	2·590	2·63	2·45

Cochran's (1953) very precise values for salicylic acid and Downie & Speakman's (1954) data from ammonium hydrogen disalicylate hydrate. This last compound was interpreted as containing both molecules

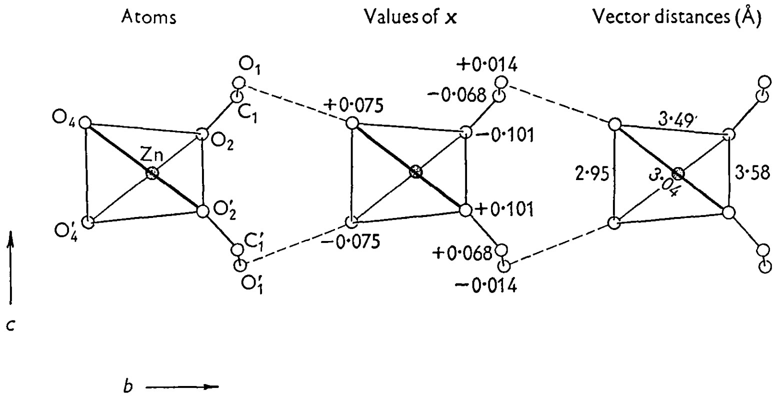

Fig. 5. One of the strings of Zn–O tetrahedra parallel to the *b* axis.

of free salicylic acid and salicylate radicals, and bond distances were estimated to be correct within 0·05 Å. The anion, A^-, comparisons of Table 4 are entirely satisfactory, although the discrepancies for C_1–O_2 and O_1–O_2 are unexpectedly large.

Except for atoms O_1 and O_3, the entire salicylate radical is planar within the accuracy of the atomic positions. The plane of the radical satisfies the equation:

$$1{\cdot}1200x + 1{\cdot}0606y - 1{\cdot}9664z = 1 \,,$$

where x, y, and z are the parameters of the atoms. Atom O_1 is approximately 0·17 Å out of the plane of the radical in the direction of the O_4 water oxygen to which it is bonded. The strength of this bond, as evidenced by its length, 2·55 Å, may well be responsible for pulling O_1 out of the plane of the radical. O_3 is out of the radical plane about 0·12 Å in the opposite direction. This, again, is in the direction to be expected in connection with its hydrogen bond to the O_4 atom of the water molecule. The planes of the two salicylate radicals in the molecule are approximately parallel to the $(11\bar{2})$ and $(\bar{1}12)$ planes, respecspectively. More precisely, the normal to the plane of the salicylate radical (the radical approximately parallel to $(11\bar{2})$) makes an angle of 44° with the z axis, and the projection on (001) of the radical plane's direction of steepest descent makes an angle of 20° with the y axis.

3. *The* Zn–O *coordination groups*

Previous studies of several organic zinc salts have reported distorted octahedral coordinations around the zinc atom. Broomhead & Nicol (1948) reported an average Zn–O distance of 2·08 Å for the 6 H_2O about zinc in zinc benzene sulfonate hexahydrate. Hargreaves (1957) found Zn–O distances of 2·05, 2·08, and 2·14 Å in the nearly regular octahedron of 6 H_2O about zinc in zinc *p*-toluene sulfonate hexahydrate. Merritt, Cady & Mundy (1954) found two Zn–O distances of 2·05 and 2·27 Å and two Zn–N distances of 2·06 Å in zinc 8-hydroxyquinolate dihydrate. Finally, in zinc acetate dihydrate distances of 2·14, 2·17, and 2·18 Å were found in the badly distorted Zn–O octahedron (van Niekerk, Schoening & Talbot, 1953).

Despite these previous findings, the first sphere of coordination in zinc salicylate dihydrate is clearly tetrahedral. The two water oxygens, O_4's, at 2·06 Å, and the two O_2 carboxyl oxygens at 2·03 Å form a slightly distorted tetrahedron about the zinc. A string of these Zn–O tetrahedra along the *b* axis is illustrated in Fig. 5. These two nearly identical Zn–O distances are in good agreement with the smaller of the Zn–O distances reported above, and are only slightly larger than the sum (1·97 Å) of the tetrahedral covalent radii for Zn and O (Pauling, 1939). Tetrahedral coordination of oxygen around zinc is found, of course, in the well known ZnO structure with Zn–O distances of 1·95 and 1·98 Å (Wyckoff, 1948). In zinc salicylate dihydrate, as in ZnO, some ionic character is expected in the Zn–O bonds. Hybridization of the $4s$, $4p^3$ orbitals would provide the necessary tetrahedral bonding orbitals.

The remaining two carboxyl oxygens, O_1's, are situated at a much greater distance, 2·52 Å, from the zinc atoms, so that it is hardly possible to consider them to be bonded to the zinc. It might have been expected that these remaining carboxyl group oxygens would have been pulled into the zinc coordination sphere with hybridized $4s$, $4p^3$, $4d^2$ octahedral coordination, as was suggested by Merritt *et al.* (1954) for zinc 8-hydroxyquinolate dihydrate. However, the relative instability of the $4d$ orbitals is well known, and they seem to have lost out in the competition with the hydrogen bonds of the structure. The salicylate radicals appear to have pivoted about O_2 (Fig. 3) during the formation of hydrogen bonds O_4–O_3 and O_4–O_1, thus preventing O_1 from approaching the zinc close enough for octahedral coordination.

Curiously, too, it is the carbonyl oxygens, O_2's, and not the hydroxyl oxygens, O_1's, of the carboxyl groups that have been pulled into the Zn–O coordination sphere, although the latter oxygens (from their longer C–O distances) might be expected to be the more negative. This is in line, however, with the findings of Downie & Speakman (1954) for ammonium hydrogen disalicylate hydrate, in which the ammonium ion coordinates water oxygen, carbonyl oxygens of the carboxyl groups, and oxygens of the *o*-hydroxyl groups, but not hydroxyl oxygens of the carboxyl groups.

References

Broomhead, J. M. & Nicol, A. D. I. (1948). *Acta Cryst.* **1**, 88.

Buerger, M. J. & Klein, G. E. (1945). *J. Appl. Phys.* *16*, *408*.

Clark, G. L. & Kao, H. (1948). *J. Amer. Chem. Soc.* **70**, 2151.

Cochran, W. (1953). *Acta Cryst.* **6**, 260.

Downie, T. C. & Speakman, J. C. (1954). *J. Chem. Soc.* p. 787.

Hargreaves, A. (1957). *Acta Cryst.* **10**, 191.

Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

Hughes, E. W. & Lipscomb, W. N. (1946). *J. Amer. Chem. Soc.* **68**, 1970.

James, R. W. (1954). *The Optical Principles of the Diffraction of X-rays*, pp. 180–190, 608. London: Bell.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Merritt, L. L., Cady, R. T. & Mundy, B. W. (1954). *Acta Cryst.* **7**, 473.

Niekerk, J. N. van, Schoening, F. R. L. & Talbot, J. H. (1953). *Acta Cryst.* **6**, 720.

Pauling, L. (1939). *The Nature of the Chemical Bond*, p. 167. Ithaca: Cornell University Press.

Pauling, L. & Sherman, J. (1932). *Z. Kristallogr.* **81**, 1.

Wyckoff, R. W. G. (1948). *Crystal Structures*, chap. 3, p. 31. New York; London: Interscience Publishers.

Acta Cryst. (1958). **11**, 46

Thermocrystallography of Higher Hydrides of Titanium and Zirconium*

By H. L. Yakel, Jr.

Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.†

(*Received* 18 *January* 1957 *and in revised form* 10 *June* 1957)

Low- and high-temperature X-ray diffraction investigations of titanium dihydride ($TiH_{1.99}$) and dideuteride ($TiD_{1.98}$) have indicated apparent 'second-order transformations' in both substances below a critical temperature of 310° K. The tetragonal low-temperature phases are distortions of the cubic fluorite high-temperature phases, and are isomorphous with the tetragonal ZrH_2 structure. A similar study of zirconium dihydride ($ZrH_{1.92}$) has shown that the tetragonality of the lattice of this substance is also temperature-dependent. The critical temperature of the 'second-order transformation' in $ZrH_{1.92}$ is unattainable in the present diffraction apparatus owing to dissociation of the hydride. Possible causes of the transformations are discussed.

Introduction

Many fundamental studies of solid metallic hydrides have been stimulated by the chemical nature of these materials, which seemingly is intermediate between that of interstitial alloys and inorganic compounds. This interest has recently been augmented by practical applications of solid hydrogeneous materials in the field of nuclear engineering.

In particular, investigations of the crystal structures of the hydrides of the Group IV *A* elements, and the relation of their structures to chemical and physical properties, extend from the early work of Hägg (1931) on titanium and zirconium hydrides to the recent study of the zirconium–hydrogen system by Vaughan & Bridge (1956) in which high-temperature X-ray diffraction methods were used. Phase diagrams of the titanium–hydrogen and zirconium–hydrogen systems have been presented by Lenning, Craighead & Jaffee (1954) and Vaughan & Bridge (1956), respectively. No diagrams for the hafnium–hydrogen or thorium–hydrogen systems have been published, but, in view of the results of diffraction studies of these hydrides by Sidhu & McGuire (1952) and Rundle, Shull & Wollan (1952), a general similarity with the titanium- and zirconium–hydrogen systems is likely.

The crystal structures of the hydride 'compounds' which exist at compositions between MH and MH_2 (where M is a IV A metal) all appear to be based on a face-centered cubic, or face-centered tetragonal*, array of metal atoms with hydrogen atoms located in

---

* A preliminary report of this investigation was presented under the title 'Apparent Second-Order Phase Transformations in Titanium Dihydride and Dideuteride' at the Thirteenth Annual Pittsburgh Diffraction Conference, 3 November 1955.

† Operated by the Union Carbide Nuclear Company for the United States Atomic Energy Commission.

* Descriptions of these structures in terms of face-centered rather than body-centered tetragonal lattices will be retained throughout this paper for purposes of comparison with the cubic fluorite structure.