

by a root mean square distance of 0.055 Å of atoms C(7), C(8), C(9), and C(11) from the mean plane $B3-C1$ ($0.777x + 0.532y - 0.335z - 5.049 = 0$). Planes $C3$ and $D1$, however, are less similar in this respect, since they have an interplane angle of 167° , and since atoms C(12), C(13), C(14), and C(15) have a root mean square distance of 0.076 Å from the mean plane of $C3-D1$ ($0.715x + 0.510y - 0.479z - 2.602 = 0$).

The stacking diagram for 4-bromoestradiol parallel to the x - y plane is shown in Fig. 3. The numbers beside each atom represent the height of the atom along z . The molecules are joined together in quasi-polymeric chains parallel to the x axis by hydrogen bonds between O(3) and O(17) which are 2.87 Å long. The position of the methanol group is stabilized by

Table 9. Distances of closest approach less than 4.000 Å

x direction		z direction	
O(3)-O(17)	2.869	C(1)-C(6)	3.848
O(3)-O(methanol)	2.604	C(3)-O(methanol)	3.450
O(17)-O(methanol)	2.736	C(4)-C(14)	3.993
C(2)-C(methanol)	3.652	C(7)-Br	3.966
C(3)-O(17)	3.908	C(18)-C(12)	3.921
C(3)-C(methanol)	3.517	C(18)-C(11)	3.755
C(4)-C(methanol)	3.750	O(3)-C(methanol)	3.337
C(16)-Br	3.698	O(3)-C(7)	3.689
C(17)-Br	3.847	Br-C(2)	3.845
C(17)-O(methanol)	3.751	C(methanol)-O(17)	3.851
O(3)-C(17)	3.459		
O(3)-C(methanol)	3.823		
y direction			
C(6)-C(15)	3.756		
C(6)-C(16)	3.709		
C(7)-O(3)	3.689		
C(12)-C(18)	3.921		
Br-C(15)	3.727		

two hydrogen bonds. One of these is 2.60 Å in length and joins the methanol oxygen atom to the phenolic oxygen atom, O(3). The other is 2.74 Å long and bonds the methanol oxygen atom to the hydroxyl oxygen atom, O(17). Numerous van der Waals interactions hold the molecules together in the x -, y -, and z -directions. Table 9 shows the various distances of closest approach less than 4.000 Å.

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Atomic Coordinates of $AlPO_4$

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The X-ray powder diffraction data on $AlPO_4$ have been obtained on a diffractometer. The system is found to be trigonal with cell constants $a = 4.941$ Å, $c = 10.95$ Å and space group $P3_121$. From the known similarity between $AlPO_4$ and α -quartz, the atomic coordinates have been determined to be

$$\begin{aligned} O(1): & x = 0.275, y = 0.406, z = 0.118 \\ O(2): & x = 0.275, y = 0.406, z = 0.600 \\ Al: & x = 0.500 \\ P: & x = 0.500 \end{aligned}$$

The reliability index is 0.16.

Introduction

The study of compounds similar to quartz is a subject of considerable interest; Buerger (1948, 1954) has dis-

cussed the physico-chemical basis of the structure of such compounds in detail. The structure of aluminum phosphate which is iso-electronic with quartz is of still greater interest. According to Buerger (1948), $AlPO_4$ is a half-breed derivative of quartz in which half of the Si positions are occupied by trivalent

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atoms Al and half by pentavalent atoms P. The similarity between quartz and AlPO_4 has also been established from the piezoelectric measurements (Mason, 1950), microscopic optical studies (Gruner, 1945), studies of thermal polymorphic transformations (Papailhau, 1955; Trömel & Winkhaus, 1957), effect of impurities on transformations and the stability of polymorphs (Winkhaus, 1951) and thermal and crystallographic studies (Hummel, 1949; Perloff, 1956). It is now definitely known that all the low and high temperature modifications corresponding to quartz, tridymite and cristobalite are known in AlPO_4 (Beck, 1949; Hummel, 1949; Papailhau, 1955).

The first X-ray crystal-structure study of AlPO_4 was made by Strada (1934), who reported a tetragonal structure for it. This form is not known in quartz. Since then it has not been possible to produce the laboratory conditions congenial to the growth of the tetragonal modifications. The cristobalite modification was obtained by Caglioti (1935) and its structure has been worked out in detail by Mooney (1956). The cell constants corresponding to the α -quartz modification have been found out by Huttenlocher (1935) and the bond type and the z coordinates for this modification have been determined by Brill & deBretteville (1948, 1955). In the present work the complete structure of AlPO_4 corresponding to the α -quartz form has been worked out and the details are presented below.

Experimental

The great difficulty of growing single crystals of AlPO_4 has compelled us to resort to the X-ray powder technique. The powder was obtained from Riedel De Haen, Germany. For the purpose of taking an X-ray photograph the sample was ground to about 200 mesh, and by mixing it with gum tragacanth a thin cylindrical specimen was prepared. The X-ray photographs of this sample were taken on a Philips Debye Scherrer camera of diameter 11.46 cm with Straumanis mounting by using $\text{Cu } K\alpha$ radiation from a Philips X-ray generator. A photograph was also taken of an air-quenched sample heated to 1000 °C. For comparison, α -quartz photographs were also taken under similar conditions (Sharan, 1954). This showed a complete resemblance between the photographs of the two substances. The unheated aluminum phosphate photograph was indexed on the basis of the α -quartz structure, which is trigonal. The mean values of the cell constant as determined from the high angle $\text{Cu } K\alpha_1$, $K\alpha_2$ resolved doublets are

$$a = 4.941_6 \text{ \AA}; \quad c = 10.95_7 \text{ \AA}.$$

The values are slightly different from those obtained by earlier workers (Huttenlocher, 1935; Brill & deBretteville, 1948). In the reflexions of $00l$ type, only those with $l=3n$ are present, and this suggests that the space group belongs to one or other of the enantiomorphic groups $P3_121$ or $P3_221$, with point group 32. Following earlier workers and from the

similarity of observations, we take the number of molecules per unit cell as three.

Table 1. Observed and calculated structure factors

hkl	F_{obs}	F_{calc}	$F_{\text{calc}} \times \exp[-B \sin^2 \theta / \lambda^2]$	$ F_{\text{o}} - F_{\text{c}} $
100	20	28	28	8
101	12	12	12	0
003	11	13	13	2
102	53	55	55	2
110	29	32	32	3
104	31	29	29	3
112	17	19	19	2
200	28	40	39	11
202	28	36	36	8
210	—	3	3	3
212	29	26	26	3
116	14	10	10	4
300	18	17	17	1
108	46	46	45	1
304	30	33	31	1
220	31	32	30	2
118	25	29	27	2
310	38	41	38	0
312	16	13	13	3
208	23	14	14	9
314	17	21	19	2
400	29	29	27	2
10,1,0	24	23	21	3
10,1,2	16	16	15	1
226	35	40	36	1
308	25	26	23	2
320	24	24	22	2
11,1,0	29	28	23	4
322	24	23	20	4
20,1,2	19	23	19	0
410	—	7	7	7
302	12	11	11	1
228	12	11	10	2
21,1,0	16	17	15	1
21,1,2	10	14	12	2
318	23	22	21	2
414	22	21	18	4
30,1,0	—	7	6	6
326	15	10	9	5
500	14	13	12	2
502	20	22	19	1
408	14	14	12	2
416	—	8	7	7
330	18	18	15	3
22,1,0	12	8	7	5
332	12	21	17	5
504	25	33	27	2
420	14	20	16	2
31,1,0	11	20	16	5
422	—	5	4	4

For quantitative work, the peak intensities were measured on a Philips diffractometer. After scaling the relative intensities suitably, the values of F_{obs} were calculated from the formula

$$I \propto p F_{\text{obs}}^2 (1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$$

and are given in Table 1. Here p is the multiplicity factor, $(1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$ is the Lorentz polarization factor whose values were taken from tables in Henry, Lipson & Wooster (1953) and θ the Bragg angle. As the specimens used for the diffraction work were very thin and of low absorption, no attempt has been made to apply the absorption correction.

Structure analysis

The analysis has been based on the space group $P3_121$. The coordinates of the equivalent points are (*International tables for X-ray crystallography*, 1952):

General

$$c \quad x, y, z; \bar{y}, x-y, \frac{1}{3}+z; y-x, \bar{x}, \frac{2}{3}+z; \\ y, x, \bar{z}; \bar{x}, y-x, \frac{1}{3}-z; x-y, \bar{y}, \frac{2}{3}-z.$$

Special

$$b \quad x, 0, \frac{1}{3}; 0, x, \frac{2}{3}; \bar{x}, \bar{x}, 0; \\ a \quad x, 0, \frac{5}{6}; 0, x, \frac{1}{6}; \bar{x}, \bar{x}, \frac{1}{2}.$$

The unit cell contains three mols of AlPO_4 . Accordingly Al and P are expected to be distributed in the special positions *a* and *b* and O in groups of two in general position *c*.

The *c* axis has about twice the value found in quartz but the weakness of the general reflexions from planes with odd values of *l* means that there are scattering units half way along the *c* axis. This is consistent with the isomorphism of AlPO_4 with quartz. This can be seen by putting the molecular formula of quartz as SiSiO_4 , which immediately suggests that for isomorphism in the structures, alternate tetravalent Si^{4+} must be replaced by trivalent Al^{3+} and pentavalent P^{5+} . It implies that in AlPO_4 the *a* axis remains the same and the *c* axis becomes double that in quartz. If this be so, then to a first approximation, there should be two types of oxygen, having the same *x, y* coordinates and *z* differing by $\frac{1}{2}$. Similarly only the *z* coordinates of Al and P should differ, the difference being $\frac{1}{2}$. This analysis qualitatively explains the observed facts.

In order to decide the ionic characters of AlPO_4 , Brill & deBretteville (1955) measured the absolute value of the F_{003} reflexion and concluded that aluminum, phosphorus and oxygen should be trivalent, pentavalent and divalent respectively. Following the above authors and the chemical evidence we have used the *f* values for Al^{3+} , P^{5+} and O^{2-} in the present calculations.

The complete structure of low quartz and aluminum orthoarsenate has been worked out by Machatschki (1936). As the properties of AlPO_4 are expected to be in between those of quartz and AlAsO_4 , as a preliminary we chose the mean values of the coordinates for the calculations of the structure factors of AlPO_4 . The *R* value was 0.30.

It was found impossible to improve the *R* value significantly. Several alternative models were tried. One of these was based on $P3_221$, while the positions of Al and P were interchanged in the other. Trial calculations with *hk0* reflexions showed a greater divergence from the experimental values. This failure led us to believe that there might be a slight departure from the midway interleaving of the oxygen ions, i.e., the second type of oxygen ions might not be exactly half way up the first type along the *c* axis

but might be slightly off. The evidence in favour of this is as follows:

1. The intensity of the 10.1 reflexion, on the midway structure, should be very weak, but the fact that it is stronger can be explained only by another alternative.
2. Since Al-O and P-O bindings must be different, their distances must also be different. This has been confirmed by infrared studies on AlPO_4 , AlAsO_4 and SiO_2 (Saksena, 1957).

Accordingly, the difference in the *z* coordinates of the two types of general oxygen atoms was changed to 0.482. This showed some improvement. Successive trials were made by varying the coordinates slightly. The final trial with an empirical value of $B=0.5$ in the Debye-Waller factor $\exp(-B \sin^2 \theta / \lambda^2)$ for temperature correction yielded an *R* value of 0.16. It has not been possible to improve it further. F_{obs} and F_{calc} are given in Table 1 for comparison. The final coordinates fixed by us are

$$\text{O}(1): \quad x_1=0.275, \quad y_1=0.406, \quad z_1=0.118; \\ \text{O}(2): \quad x_2=0.275, \quad y_2=0.406, \quad z_2=0.600; \\ \text{Al}: \quad x=0.500; \\ \text{P}: \quad x=0.500.$$

The *z* coordinates are the same as found by Brill & deBretteville (1955) with a different origin.

It is difficult to calculate F_{obs} separately for those reflexions which appear at the same angle. For such reflexions the total I_{obs} and I_{calc} have been compared and are given in Table 2.

Table 2. Calculated and observed intensities of overlapping reflexions I_c and I_o

<i>hkl</i>	I_o	F_c	I_c
006 } 114 }	10	23 28	9
106 } 204 }	5	31 16	5
222 } 216 }	2.5	11 28	3.5
224 } 306 }	1	14 15	1
206 } 214 }	10	61 32	15
406 } 324 } 412 }	2	38 8	3
		13	
402 } 218 }	2	13 22	2
316 } 404 }	1	14 5	0.7

As a further check the *F* values of the unobserved reflexions corresponding to odd values of *l* were also calculated. These were always found to be too small to be given here.

The experimental structure factors of $000l$ were

measured by Brill & deBretteville (1955) with a single crystal up to $l=24$. The geometry of our apparatus did not enable us to observe the orders above $l=6$. Since our z coordinates have been taken to be the same as theirs, our calculated values for these reflexions are the same and are expected to show the same measure of agreement.

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X-ray Studies of the Bis-*N*-alkylsalicylaldiminates of Bivalent Metals. II. Structure of Bis-*N*-ethylsalicylaldimine-palladium

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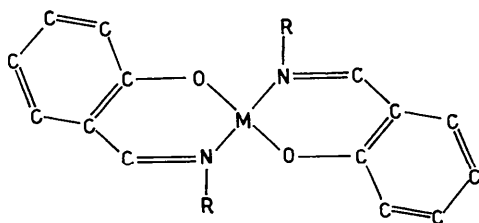
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In the course of the examination of the metal-complexes of *N*-*R*-salicylaldimines (R = alkyl), the crystal structure of bis-*N*-ethylsalicylaldimine-palladium was determined by two-dimensional Fourier methods.

The unit cell is monoclinic with lattice constants: $a = 8.43$, $b = 5.60$, $c = 17.97$ Å; $\beta = 94^\circ 42'$; $Z = 2$. The space group is $P2_1/c$. The metal atoms are required to be at symmetry centres and the bonds around the palladium are in a trans-planar arrangement. The chelate ring does not lie in a plane.

Introduction

In the series of complexes of bis-*N*-*R*-salicylaldimines with bivalent metals with the general formula:



the refined structure has been determined only for the

complexes of bis-*N*-methylsalicylaldimine with nickel (Frasson, Panattoni & Sacconi, 1959) and copper (Meuthen & Stackelberg, 1960; Lingafelter, Morosin & Simmons, 1960).

Preliminary informations on the structure of numerous complexes of the series with R = *n*-alkyl have been recently given by Frasson & Panattoni (1962). For most complexes the square planar coordination was demonstrated. Sacconi, Orioli, Paoletti & Ciampolini (1962) have examined some complexes of the series in which R = branched alkyl. For the isopropyl complexes of nickel, copper and cobalt they found evidence for tetrahedral coordination by comparing the absorption spectra of these complexes with the spectra