The Crystal Structure of Dicalcium Phosphate, CaHPO₄

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Anhydrous dicalcium phosphate has been found to be triclinic with space group $P\bar{1}$, the cell dimensions being

$$a = 6{\cdot}90 \pm 0{\cdot}01, \quad b = 6{\cdot}65 \pm 0{\cdot}01, \quad c = 7{\cdot}00 \pm 0{\cdot}01 \text{ Å};$$
$$\alpha = 96° 21', \quad \beta = 103° 54', \quad \gamma = 88° 44'.$$

The atomic coordinates have been found by analysis of the three-dimensional Patterson function, and the structure has been refined to a residual error factor $R = 0{\cdot}20$. The structure contains independent PO₄ groups, one kind of calcium atom having a coordination of seven and the other of eight oxygens. Visual estimates of intensities were employed and the errors in these are considered to be too large to enable the positions of the hydrogen atoms to be found.

Introduction

The crystal structure of anhydrous dicalcium phosphate, CaHPO₄, (calcium hydrogen phosphate, or monetite) was investigated as part of a programme of research into phosphate structures of interest both in fertilizer manufacture and in the complex subject of phosphate fixation in the soil. A description of the structure of dicalcium phosphate dihydrate, CaHPO₄. 2H₂O, has already been given (Beevers & Raistrick, 1954). The work is being undertaken in collaboration with the Research Department of Scottish Agricultural Industries Ltd.

The substance CaHPO₄ is of particular interest as it is the form present in several mixed fertilizers, especially those in whose manufacture nitric acid and/or free ammonia are used. It is hoped that the work, of which this structure determination is a part, will help to make more intelligible the changes which occur during manufacture and in the soil, and especially to clarify the nature of the solids deposited from solution with Ca/P ratios in the range between 1·0 (dicalcium phosphate) and 1·66 (hydroxyapatite).

Experimental

According to Groth (1908) anhydrous dicalcium phosphate is triclinic pinacoidal. Exceptionally pure prismatic crystals of maximum size 0·5 mm. were kindly made available by the Research Department of the Tennessee Valley Authority. Oscillation and Weissenberg photographs about the principal axes were obtained, using Cu $K\alpha$ radiation and a 5 cm.-radius normal-beam Weissenberg camera. The unit-cell dimensions were obtained from high-order $0kl$, $h0l$ and $hk0$ reflexions. The results were

$$a = 6{\cdot}90 \pm 0{\cdot}01, \ b = 6{\cdot}65 \pm 0{\cdot}01, \ c = 7{\cdot}00 \pm 0{\cdot}01 \text{ Å};$$
$$\alpha = 96° 21', \ \beta = 103° 54', \ \gamma = 88° 44'.$$

These agree with the values previously obtained by Lehr, Smith & Brown (1952).

The cell contains four molecules of CaHPO₄, giving a calculated specific gravity of 2·92, compared with observed values of 2·93 (de Schulten) and 2·89 (Bassett). The space-group is $P\bar{1}$, and we have confirmed the presence of the morphological centre of symmetry by the statistical test of Howells, Phillips & Rogers (1950).

The reflexion intensities were estimated by visual comparison, using multiple exposures, and were corrected for Lorentz and polarization factors. The small irregular crystals precluded any correction for the rather high absorption. An attempt was made to place the intensities for the three two-dimensional zones on an absolute scale by Wilson's method, but this proved unsatisfactory, probably because of the absorption effect. The latter also prevented any measurement of the temperature factor. The general intensities were therefore left on a relative scale.

Structure determination

In the space group $P\bar{1}$ the general positions are twofold, and, since there are two CaHPO₄ molecules in the unique volume of the cell, all the atoms can be in general positions. Since there are only four unique heavy atoms, giving rise to sixteen interatomic vectors, Patterson methods seemed promising. The three Patterson projections down the principal axes were computed, but the occurrence of many almost coincident vectors made their interpretation impossible.

A three-dimensional Patterson function over the unique half of the cell was therefore calculated, using an electrical analogue computer of the Hägg–Laurent type, built by Dr F. Stern. Intervals of 30ths of the cell edges were used, and the resulting function was drawn out in 16 sections parallel to the *b–c* plane. A list was drawn up of the principal vectors, and a

Table 1. *Values of F_o and F_c for the* (hk0), (h0l), (0kl) *and* (hk3) *planes of* CaHPO$_4$

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$_c$	hkl	F$_o$	F$_c$	hkl	F$_o$	F$_c$	hkl	F$_o$	F$_c$	hkl	F$_o$	F$_c$	hkl	F$_o$	F$_c$
010	0	1̄	230	0	1	500	29	3̄0	810	14	20	207	4	8	406	19	1̄5	707	28	1̄7	0̄6̄2	38	38	055	34	4̄3	213	64	65	3̄3̄3	13	7̄
020	32	25	2̄4̄0	39	41	510	21	2̄0	820	3	7	208	0	1	407	16	15	801	28	1̄3	0̄7̄2	10	1̄2	065	20	17	313	0	1	4̄3̄3	0	7
030	51	5̄1	2̄5̄0	27	2̄0	520	37	3̄8	830	10	15	2̄0̄1	54	6̄4	408	5	2	80̄1	20	17	0̄8̄2	7	7̄	0̄1̄5	11	6	413	42	3̄6	5̄3̄3	0	0
040	33	3̄1	2̄6̄0	35	32	530	12	6̄	8̄1̄0	12	1̄2	20̄2	78	77	501	36	3̄3	80̄2	23	28	013	0	0	0̄2̄5	19	1̄6	513	0	5̄	6̄3̄3	28	3̄4
050	23	14	2̄7̄0	12	8̄	5̄4̄0	8	9̄	8̄2̄0	16	1̄8	20̄3	0	2	502	35	30	803	33	3̄7	023	30	3̄1	0̄3̄5	0	6̄	613	32	27	733	0	8
060	10	7	2̄8̄0	15	12	550	28	27	8̄3̄0	7	3̄	20̄4	38	3̄7	503	7	6	80̄4	16	1̄9	033	44	3̄7	0̄4̄5	6	6	713	20	18	1̄4̄3	24	1̄8
070	6	6̄	300	24	18	560	27	29	001	21	2̄0	20̄5	0	1̄	504	20	2̄0	805	30	31	043	67	5̄7	0̄5̄5	21	20	1̄1̄3	24	3̄1	1̄4̄3	6	8
080	16	2̄4	310	47	4̄4	5̄1̄0	0	3	002	62	8̄9	20̄6	8	9	505	0	6̄	011	10	10	053	33	29	0̄6̄5	21	1̄6	2̄1̄3	27	3̄5	2̄4̄3	35	1̄9
100	0	2	320	21	2̄3	5̄2̄0	8	9̄	003	53	63	20̄7	0	3̄	50̄1	0	7	021	14	1̄4	063	5	5̄	0̄7̄5	23	2̄1	313	29	18	3̄4̄3	0	3
110	0	3	330	16	14	530	6	8	004	20	20	20̄8	0	3	50̄2	18	2̄2	031	15	8	073	29	34	016	46	52	4̄1̄3	21	20	4̄3̄3	0	7̄
120	64	83	340	12	12	5̄4̄0	25	2̄7	005	9	1̄0	301	46	47	50̄3	40	30	041	40	32	0̄1̄3	40	4̄1	026	0	2	513	0	5	5̄4̄3	6	7
130	42	4̄0	350	25	1̄5	550	0	9̄	006	0	1̄	302	0	4̄	50̄4	0	5	051	24	1̄5	0̄2̄3	23	1̄4	036	0	2	613	0	6̄	6̄4̄3	30	2̄7
140	5	0	360	30	2̄7	5̄6̄0	24	20	007	0	7	303	28	2̄2	50̄5	42	3̄9	061	39	46	0̄3̄3	50	4̄7	046	0	9̄	713	0	0	7̄4̄3	0	3
150	5	3	370	19	1̄1	600	30	34	008	0	2̄	304	11	9	50̄6	17	1̄4	071	16	1̄7	0̄4̄3	16	22	056	22	24	8̄1̄3	0	1̄	153	29	1̄9
160	23	18	3̄1̄0	28	2̄9	610	0	7	101	19	1̄9	305	38	36	50̄7	18	12	081	9	1̄2	0̄5̄3	18	12	0̄1̄6	24	23	123	69	69	1̄5̄3	53	50
170	29	20	3̄2̄0	88	93	620	0	5̄	102	49	4̄5	306	0	6̄	50̄8	14	1̄0	0̄1̄1	15	16	063	62	61	0̄2̄6	38	39	223	23	20	2̄5̄3	44	4̄3
180	19	19	3̄3̄0	0	7̄	630	18	1̄3	103	18	24	307	28	3̄8	601	55	53	0̄2̄1	19	20	0̄7̄3	0	0	0̄3̄6	37	3̄7	323	74	6̄6	3̄5̄3	37	2̄1
1̄1̄0	0	6̄	3̄4̄0	47	54	640	32	3̄6	104	21	25	30̄1	22	22	602	14	1̄6	031	50	60	083	12	14	0̄4̄6	0	8̄	423	0	4	4̄5̄3	0	6
1̄2̄0	69	9̄3	3̄5̄0	11	1̄0	650	11	11	105	20	1̄3	30̄2	17	18	603	19	1̄7	0̄4̄1	39	4̄5	014	34	38	056	27	2̄7	523	20	14	5̄5̄3	0	8̄
1̄3̄0	24	23	3̄6̄0	5	5̄	660	12	1̄3	106	5	5̄	30̄3	0	3̄	604	16	11	051	8	7̄	024	8	1̄1	0̄6̄6	24	22	623	10	1̄6	6̄5̄3	0	3
1̄4̄0	7	6̄	3̄7̄0	0	1̄	6̄1̄0	0	0	107	4	5	30̄4	42	39	60̄1	53	7̄0	0̄6̄1	60	6̄0	034	0	2̄	017	31	3̄3	1̄2̄3	70	8̄1	1̄6̄3	35	25
1̄5̄0	25	15	400	5	4	6̄2̄0	8	8̄	108	0	3	30̄5	12	15	60̄2	9	6	0̄7̄1	6	8	044	0	5	027	14	1̄2	2̄2̄3	36	42	2̄6̄3	0	0
1̄6̄0	6	2	410	17	1̄6	6̄3̄0	23	2̄6	10̄1	9	5̄	30̄6	40	3̄8	60̄3	61	75	081	0	2	054	0	6̄	037	0	5	323	0	2̄	3̄6̄3	37	3̄5
1̄7̄0	29	2̄0	420	20	22	6̄4̄0	18	18	10̄2	31	25	30̄7	4	1̄5	60̄4	19	1̄8	012	26	25	064	9	7̄	047	15	1̄3	4̄2̄3	0	1̄2	4̄6̄3	24	2̄7
1̄8̄0	16	1̄7	430	19	22	650	0	0	10̄3	48	4̄7	30̄8	23	22	60̄5	17	1̄3	022	39	3̄2	074	16	1̄0	0̄1̄7	17	1̄7	5̄2̄3	51	64	1̄7̄3	10	2̄6
200	78	8̄8	440	23	22	6̄6̄0	56	59	10̄4	40	2̄5	401	55	5̄5	60̄6	19	22	032	29	19	0̄2̄4	60	66	0̄2̄7	25	26	6̄2̄3	0	3	2̄7̄3	34	1̄3
210	13	8	450	8	11	700	10	19	10̄5	14	13	402	10	4	60̄7	0	8̄	042	17	15	0̄3̄4	37	36	037	0	8̄	7̄2̄3	34	4̄3			
220	16	1̄7	460	7	13	710	18	27	10̄6	9	12	403	34	32	701	4	7	052	21	1̄5	0̄4̄4	34	2̄5	0̄4̄7	22	1̄6	8̄2̄3	0	10			
230	6	4	470	22	1̄5	720	30	39	10̄7	0	0	404	18	11	702	28	2̄2	062	0	7	0̄5̄4	22	20	057	8	1̄3	133	42	4̄3			
240	0	8̄	4̄1̄0	19	1̄9	730	9	1̄0	10̄8	0	5	405	16	1̄1	703	0	4	072	15	13	0̄6̄4	34	3̄9	018	10	1̄4	233	38	42			
250	41	3̄1	4̄2̄0	0	6	740	0	3̄	201	62	72	406	0	2̄	70̄1	9	1̄4	082	18	27	0̄7̄4	25	25	028	8	10	333	30	40			
260	35	3̄5	4̄3̄0	11	11	7̄1̄0	0	1	202	6	7̄	40̄1	55	59	70̄2	0	9̄	0̄1̄2	9	8	015	50	47	0̄1̄8	30	3̄0	433	20	17			
270	10	11	4̄4̄0	28	2̄9	7̄2̄0	18	2̄5	203	58	6̄1	40̄2	55	4̄3	70̄3	8	1̄2	022	47	6̄1	025	26	27	028	5	8	533	15	1̄2			
280	19	20	4̄5̄0	0	2̄	730	5	1̄0	204	0	9	40̄3	39	3̄8	70̄4	4	8	032	6	6̄	035	0	1	038	0	10	633	0	8̄			
2̄1̄0	21	21	4̄6̄0	47	4̄8	7̄4̄0	16	15	205	18	13	40̄4	44	44	705	20	21	0̄4̄2	12	17	045	33	40	0̄4̄8	30	26	1̄3̄3	35	35			
2̄2̄0	25	19	4̄7̄0	15	14	800	33	4̄2	206	0	6̄	40̄5	17	2̄0	706	0	2̄	052	0	1				1̄1̄3	7	6	2̄3̄3	27	18			

preliminary attempt was made to recover the fundamental set of heavy atoms from them by trial and error. This failed, as in many previous instances, and the vector-convergence method of Beevers & Robertson (1950) was adopted. This involved using three or more heavy atoms to search for the relative positions of the remainder in the cell, and then noting the centre of symmetry, and hence the absolute positions by inspection. Heavy atoms were assumed to lie at the Patterson origin and at two other outstandingly high peaks, and the Patterson function was superposed over the entire cell with these positions in turn as origin. The coincidence of vectors at once revealed the other five heavy atoms and the centre of symmetry, showing that the original two vectors had been correctly chosen. Moreover, by observing the peak heights carefully, Ca and P atoms were unambiguously separated.

It yet remained to discover the sixteen O atoms. The number of recorded coincidences of medium height corresponding to possible oxygen positions was confusingly large, and a further superposition with a fourth heavy atom failed to simplify the choice. The fact that the P–O distance is approximately 1·6 Å was therefore used. Spheres of this radius were constructed round the four P atoms, and all coincident vectors within about 0·2 Å of the spheres were noted. Pairs of these which were related by the previously-found centre of symmetry were then picked out. Nine pairs were in fact found, of which one corresponded to an atom in a sterically impossible position near the centre, and the remaining eight gave convincing PO$_4$ tetrahedra with no gross packing difficulties. All the vectors between the heavy atoms and the oxygens chosen were then calculated and compared with the
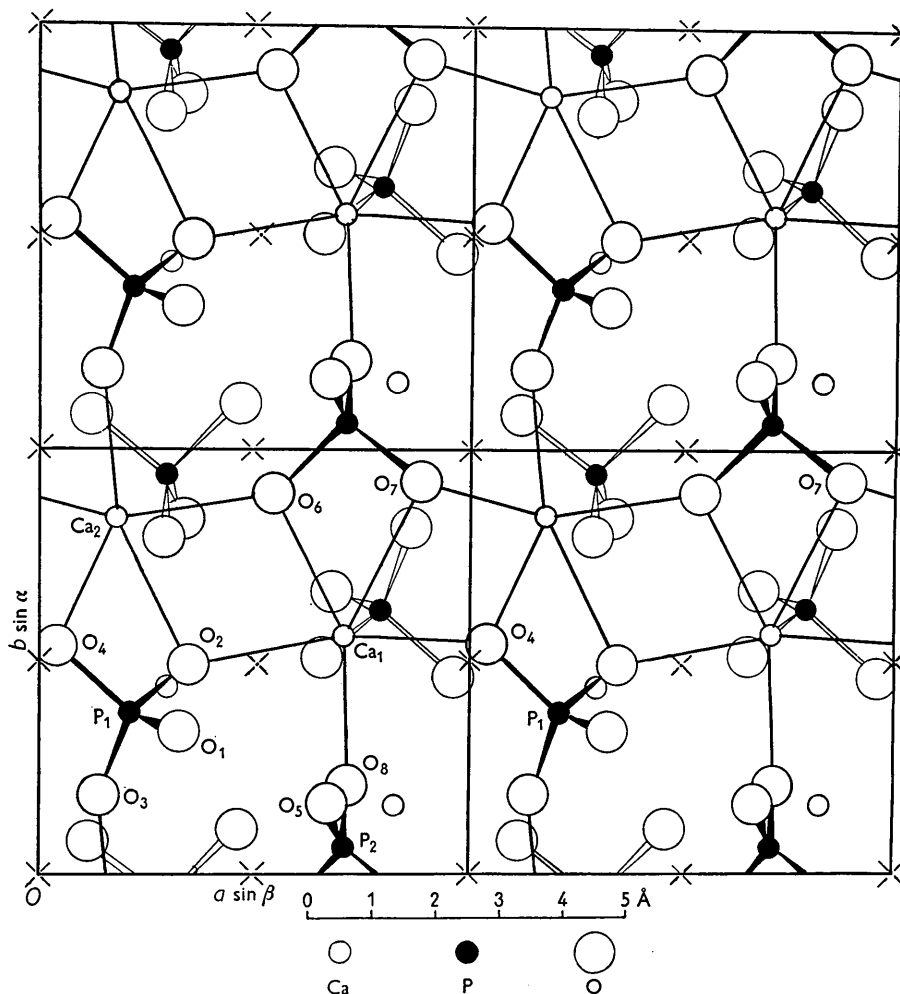
Fig. 1. Four unit cells of CaHPO$_4$, projected down the c axis.

original Patterson function to ensure not only that all the vectors were present, but that no significant peaks on the map remained unaccounted for. This was confirmed, and small alterations were then applied to the atomic positions to obtain the best possible overall fit.

Refinement

The atomic positions obtained were used to calculate structure factors for the (0kl) zone. This gave encouraging agreement, the factor $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ being 0·40. A Fourier projection, using the 77 F_o terms which could be signed, showed satisfactory details and only small shifts. When these were applied R fell to 0·35. Further refinement was carried out by the use of (F_o-F_c) syntheses, F_o being first scaled to fit F_c over five ranges of sin θ, since the Wilson scaling curve was not felt to be reliable. Four stages of refinement reduced R to 0·203. It was then decided to refine the x parameters using the (hk0) zone. Structure factors calculated using the x parameters from the Patterson superposition and the already refined y parameters

gave $R = 0·51$. Five stages of refinement exactly as for the previous zone reduced this to $R = 0·196$. Finally the (h0l) zone was refined and the structure factors calculated for the three zones with the mean parameters from the three refinements. The residuals were then:

$$R(hk0) = 0·193, \ R(h0l) = 0·216, \ R(0kl) = 0·193;$$
$$\text{average } R = 0·201 .$$

These figures include reflexions of observed zero intensity, and no corrections have been applied for extinction nor for a temperature factor. As a final check of the validity of the structure, structure factors for the (hk3) planes were calculated. Satisfactory agreement was obtained with $R = 0·285$. Observed and calculated F values for the planes (hk0), (h0l), (0kl) and (hk3) are given in Table 1.

Fourier projections computed for the final structure showed the oxygen atoms badly distorted by the diffraction rings round the heavy atoms. This is to be expected when the Fourier series for atoms with no heat motion is abruptly terminated, and the effect

could be reduced by the introduction of a suitable temperature factor.

The final atomic parameters, in 360ths of the cell edges, are:

	x	y	z
Ca$_1$	106	157	98
Ca$_2$	63	302	240
P$_1$	74	135	259
P$_2$	107	339	75
O$_1$	114	120	336
O$_2$	123	177	222
O$_3$	48	66	213
O$_4$	15	192	270
O$_5$	120	300	6
O$_6$	165	39	108
O$_7$	39	27	57
O$_8$	105	285	126

The accuracy of the determination was estimated using the equations given by Cruickshank (1949). The standard deviation in electron density, $\sigma(\varrho)$, is 1·1 e.Å^{-2} on the (0kl) projection. The standard deviation in atomic coordinates in the c direction, $\sigma(z)$, is 0·006 Å for Ca, 0·011 Å for P and 0·039 Å for O. Hence the standard deviations in bond lengths are:

Ca–O = 0·039 Å ,

P–O = 0·040 Å ,

O–O = 0·055 Å ,

O–O = 0·078 Å (if related by a centre of symmetry).

Description of the structure

The structure of CaHPO$_4$ consists of discrete PO$_4'''$ tetrahedra and Ca^{++} ions, the latter coordinated by a shell of oxygen atoms. Fig. 1 shows a projection of the structure down the c axis, four unit cells being shown. In the a direction Ca$_1$ is bonded to O$_2$ and O$_4$ attached to P$_1$, while Ca$_2$ is bonded to O$_6$ and O$_7$, attached to P$_2$. In the b direction Ca$_1$ is bonded to O$_6$ and O$_7$, and Ca$_2$ to O$_2$ and O$_4$, so that a double chain of Ca–PO$_4$–Ca extends along the a axis, thus:
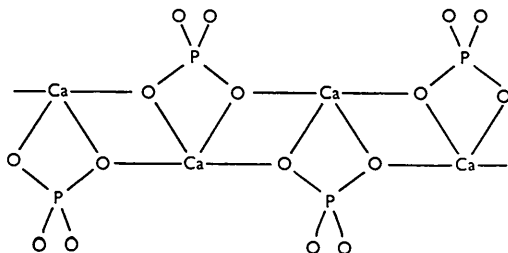
Bonds from Ca$_1$ to O$_8$ and Ca$_2$ to O$_3$ link these chains transversely in the b direction, forming a distorted sheet of atoms roughly in the (001) plane. The centre of symmetry produces a similar sheet below the first in the c direction, further bonds from Ca$_1$ to O$_1'$ and O$_2'$, and from Ca$_2$ to O$_3'$, O$_5'$ and O$_8'$ linking the sheets. Ca$_1$ thus has seven and Ca$_2$ eight nearest oxygen neighbours in its coordination shell. This variation in the calcium coordination is not unexpected. The highly electropositive nature of the metallic ion results in an unusually great ionic character in its coordination, so that no definite allocation of shared electrons from the oxygens is possible. Ca–O coordinations of all values from 6 to 9 have been reported (see Wells, 1945) and different values in the same structure have been noted where the symmetry permits (Smith, 1953).

The bond lengths and angles obtained are given in Table 2.

The average P–O bond length is 1·54 Å, the average Ca–O bond length is 2·46 Å, and the average distance O–O within the PO$_4$ group is 2·51 Å.

The two hydrogen atoms probably lie between oxygens of neighbouring PO$_4$ groups. It is not feasible to identify their positions by a reduction in the O–O distance between non-bonded atoms, since in this case, with a standard deviation of 0·055 Å in the bond length, only differences in O–O bonds greater than 0·18 are significant. This uncertainty, caused primarily by the swamping effect of the heavy atoms, is sufficient

Table 2. Bond lengths and angles

P$_1$–O$_1$ = 1·53 Å	Ca$_1$–O$_1'$ = 2·44 Å	Ca$_2$–O$_2$ = 2·58 Å
P$_1$–O$_2$ = 1·58	Ca$_1$–O$_2$ = 2·34	Ca$_2$–O$_3$ = 2·40
P$_1$–O$_3$ = 1·49	Ca$_1$–O$_2'$ = 2·48	Ca$_2$–O$_3'$ = 2·43
P$_1$–O$_4$ = 1·56	Ca$_1$–O$_4$ = 2·29	Ca$_2$–O$_4$ = 2·44
P$_2$–O$_5$ = 1·52	Ca$_1$–O$_6$ = 2·44	Ca$_2$–O$_5'$ = 2·44
P$_2$–O$_6$ = 1·56	Ca$_1$–O$_7$ = 2·69	Ca$_2$–O$_6$ = 2·51
P$_2$–O$_7$ = 1·55	Ca$_1$–O$_8$ = 2·37	Ca$_2$–O$_7$ = 2·58
P$_2$–O$_8$ = 1·54		Ca$_2$–O$_8'$ = 2·51

O$_1$–P$_1$–O$_2$ = 116·5°	O$_5$–P$_2$–O$_6$ = 111·0°
O$_1$–P$_1$–O$_3$ = 113·5	O$_5$–P$_2$–O$_7$ = 109·0
O$_1$–P$_1$–O$_4$ = 105·5	O$_5$–P$_2$–O$_8$ = 107·0
O$_2$–P$_1$–O$_3$ = 108·5	O$_6$–P$_2$–O$_7$ = 100·0
O$_2$–P$_1$–O$_4$ = 103·5	O$_6$–P$_2$–O$_8$ = 108·5
O$_2$–P$_1$–O$_4$ = 116·0	O$_7$–P$_2$–O$_8$ = 112·0

to obscure any evidence of hydrogen bonding. In fact, the shortest measured O–O contact is 2·48 Å between O$_7$ and its symmetry-related atom, where the standard deviation is higher [$\sigma(d_{12}) = 2\sigma(x_1)$] and where a hydrogen bond is not possible by space-group considerations. The next shortest contacts observed are

$$O_1–O_5 = 2·60, \quad O_6–O_8' = 2·62, \quad O_4–O_7 = 2·71 \text{ Å} .$$

The structure of CaHPO$_4$ is thus a three-dimensional network of PO$_4'''$ tetrahedra with Ca^{++} ions in the interstices, holding the anions together by highly ionic bonds with the oxygens. There seems to be no close resemblance to the structures of chemically related compounds, though CaSO$_4$, which is ortho-rhombic, has very similar cell dimensions (Dickson & Binks, 1926). In particular, the structure of apatite (Beevers & MacIntyre, 1946) is quite different, so that profound alterations in the crystal lattice must be necessary as the Ca/P ratio is reduced from 1·66, and a continuous series of solid solutions between hydroxy-apatite and anhydrous dicalcium phosphate seems unlikely.

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The Crystal Structure of Hydroxylamine

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Four molecules of hydroxylamine are in an orthorhombic unit cell of symmetry $P2_12_12_1$ and dimensions $a = 7\cdot29$, $b = 4\cdot39$, $c = 4\cdot88$ Å. The coordinates $x_O = 0\cdot060$, $y_O = -0\cdot062$, $z_O = -0\cdot023$, $x_N = 0\cdot121$, $y_N = 0\cdot244$ and $z_N = 0\cdot063$ lead to the N–O bond distance of $1\cdot47_6 \pm 0\cdot03$ Å, and to the closest intermolecular contacts of $N \cdots O = 2\cdot74$, $3\cdot07$, $3\cdot11$ and $3\cdot18$ Å. Hydrogen bonds are presumed to lie in the $2\cdot74$ and $3\cdot07$ Å contacts, thus leaving the third hydrogen atom of the molecule uninvolved, and indicating a *trans* configuration for the molecule. No residual entropy is indicated, and no transition occurs when the solid is cooled to $-185°$ C.

Introduction

Two spectroscopic investigations of hydroxylamine, one of the solid and gas by Giguère & Liu (1952), and one of the solid at low temperature by Nightingale & Wagner (1954), have recently been made. These studies differ somewhat in the observations, and the assignments of the bands are different. In particular, Nightingale & Wagner assigned the broad, intense band at 2867 cm.$^{-1}$ to a strong hydrogen bond.

In the hope that we could provide some information relating to these spectroscopic studies, and in the expectation that the structure might be closely related to those shown by hydrazine (Collin & Lipscomb, 1950, 1951), hydrogen peroxide (Abrahams, Collin & Lipscomb, 1951), methanol (Tauer & Lipscomb, 1952), and methylamine (Atoji & Lipscomb, 1953), we have carried out a study of the crystal structure as described below. Low-temperature techniques were employed partly because of the low melting point of 33° C., but chiefly because of the tendency towards rapid decomposition near room temperature.

Experimental

Hydroxylamine, prepared by the method of Hurd (1939), was transferred to a vacuum line and was partially further purified by pumping out volatile impurities for periods up to 30 min. The usual techniques of sublimation into capillaries produced impure samples, so that a modified technique was used. A section of glass tubing between the sample and vacuum pumps was drawn down to capillary diameter. With the pumps maintained in operation, a short length of this constricted region was cooled to near liquid-nitrogen temperature, allowed to warm for a short time, cooled again, with the low-temperature stream of nitrogen, and then sealed on both sides of the small slug of solid hydroxylamine. Thus prepared, the samples were stored in dry ice.

X-ray diffraction data were collected on the precession camera from a single crystal, grown with the use of a warm air stream, and maintained at $-60°$ C. during photography. Mo $K\alpha$ radiation was used, and precession angles of 21° for the $\{h0l\}$ zone and 30° for the $\{hk0\}$, $\{0kl\}$, $\{hkh\}$ and $\{2h,k,h\}$ zones were employed. No X-ray diffraction evidence of a phase transition was observable at temperatures down to $-185°$ C.

Intensities were estimated visually with the use of a standard scale of timed exposures of a reflection from a crystal of NaCl of comparable size. The usual Lorentz and polarization corrections (Waser, 1951)