Acta Cryst. (1970). B**26**, 1429

The Crystal Structure of Struvite, $MgNH_4PO_4.6H_2O$

BY A. WHITAKER* AND J. W. JEFFERY

Department of Crystallography, Birkbeck College, University of London, England

(*Received* 23 *June* 1969)

Struvite, $MgNH_4PO_4.6H_2O$ crystallizes in the orthorhombic system with cell dimensions $a=6{\cdot}941\pm0{\cdot}002$, $b=6{\cdot}137\pm0{\cdot}002$, $c=11{\cdot}199\pm0{\cdot}004$ Å. The space group is $Pmn2_1$ and there are two molecules in the unit cell. Least-squares refinement has been completed on three-dimensional data (585 structure factors within the Cu $K\alpha$ sphere). The hydrogen atoms have been found on a difference Fourier synthesis and included in the refinement with an isotropic temperature factor of 4·0. The final residual is 2·8%. The structure consists of PO_4 tetrahedra, $Mg.6H_2O$ octahedra and NH_4 groups held together by hydrogen bonding. The PO_4 tetrahedron is regular, with a mean (uncorrected) phosphorus–oxygen bond length of $1{\cdot}5370\pm0{\cdot}0011$ Å, and the $Mg.6H_2O$ octahedron is very distorted, with a mean (uncorrected) magnesium–water oxygen bond length of $2{\cdot}0711\pm0{\cdot}0011$ Å. The mean (uncorrected) water oxygen–hydrogen bond length is found to be $0{\cdot}778\pm0{\cdot}014$ Å. The thermal vibrations have been analysed and the mean corrected bond lengths are phosphorus–oxygen 1·5431, magnesium–water oxygen, 2·0810 and water oxygen–hydrogen, 0·792 Å (assuming riding motion in each case). The water oxygen–hydrogen bond length is significantly less than the internuclear separation obtained from neutron diffraction measurements. This is interpreted as being due to the electron of the hydrogen atom taking part in bond formation and so being displaced towards the bonding water oxygen atom.

Introduction

Although the mineral struvite, or guanite, has been known for a considerable time, it is not common. It occurs naturally, apparently as a result of some form of bacterial attack on organic material.

At the time this investigation commenced the X-ray data appeared to be scanty and often contradictory. The space group was variously reported as *Pmc*2 (Palache, Berman & Frondel, 1951) and $Pnm2_1$ (Bland & Basinski, 1959). The only other X-ray information found was a tentative partial structure based on a Patterson projection on one plane (Bland & Basinski, 1959).

In view of this lack of reliable X-ray data it was thought that it would be useful to check previous data and to make an accurate structure determination of this substance. In addition its low absorption suggested that the accuracy attainable would be comparatively high and might well be approaching the limit for inorganic crystal structures.

At a late stage in this investigation it was found that the structure of magnesium ammonium arsenate hexahydrate had been completed (González & de Lerma, 1955; González & García-Blanco, 1955). The space group was determined as $Pmn2_1$ (González & de Lerma, 1955) and the structure was determined from two projections. The residuals for both projections were about 20%. From a consideration of cell sizes, systematic absences and the two Patterson projections they concluded that magnesium ammonium arsenate hexahydrate and magnesium ammonium phosphate hexahydrate were isomorphous. Thus the structure of the latter could be inferred. However, these references did not come to hand (*Structure Reports for 1955,* 1963) until after the structure had been determined directly.

Experimental

Attempts to grow crystals suitable for investigation failed but finally a naturally occurring specimen was obtained by courtesy of Dr M. Rosemeyer of University College, London, who found it in a tin of salmon. It appeared to consist of a polycrystalline mass of approximate size $15\times8\times8$ mm, colourless at one end changing to a light yellow at the other. When broken open it was seen to consist of a parallel growth of columnar crystals. The crystal optics and Laue symmetry confirmed that the crystals belong to the orthorhombic system.

The cell dimensions were determined by Farquhar & Lipson's (1946) method from oscillation photographs taken with copper radiation Cu $K\alpha_1=1{\cdot}54050$, Cu $K\alpha_2=1{\cdot}54434$ and Cu $K\beta=1{\cdot}39217$ Å) and are: $a=6{\cdot}941\pm0{\cdot}002$, $b=6{\cdot}137\pm0{\cdot}002$, $c=11{\cdot}199\pm0{\cdot}004$ Å. These values are in good agreement with those reported previously (Palache *et al.*, 1951; González & de Lerma, 1955; Bland & Basinski, 1959).

D_m (by flotation) $=1{\cdot}708\pm0{\cdot}003$ g.cm^{-3}, again in good agreement with values reported previously (Mellor, 1923; Palache *et al.*, 1951 González & de Lerma, 1955; Bland & Basinski, 1959) while for $Z=2$, $D_x=1{\cdot}708\pm0{\cdot}002$ g.cm^{-3}.

Systematic absences ($h0l$ absent when $h+l=2n+1$, $h00$ absent when $h=2n+1$, $00l$ absent when $l=2n+1$)

* Now at Department of Physics, Brunel University, London.

were obtained from Weissenberg photographs and indicate the space group to be either $Pmn2_1$ or $Pmnm$.

The $N(z)$ test (Howells, Phillips & Rogers, 1949, 1950) was applied to the three-dimensional data and the crystallographic zones. This test suggested point groups $mm2$ or 222 as being most probable (the test was inconclusive for the c axis projection. Combining this with the evidence from the systematic absences, the probable space group is $Pmn2_1$. This agrees with that reported by González & de Lerma (1955) and Bland & Basinski (1959).

The $h0l$ reflexions had pseudo-hexagonal symmetry; this is due to a combination of an n-glide and the fact that the ratio $c:a$ is 1·61.

Two spherical crystals were ground, from the colourless end of the specimen, using Bond's (1951) method. Grinding proved to be difficult due to the softness and the marked anisotropy of the crystals. The commonest shape obtained approximated to a prolate sphere, the unique direction being parallel to the a axis. In addition, many ground crystals were modified by the appearance of two flat surfaces perpendicular to the b axis. This cleavage is mentioned by Palache *et al.* (1951), together with (001). The latter was not noticed but would no doubt have contributed to the shape of the ground crystals. This anisotropy would seem to imply that the atomic bonding parallel to a is stronger than in other directions.

One crystal, diameter $0·208 \pm 0·010$ mm was mounted with the a axis parallel to the fibre while a second crystal, diameter $0·199 \pm 0·011$ mm, was mounted with the b axis parallel to the fibre. After mounting, both crystals were coated with collodion to prevent decomposition (Lonsdale & Sutor, 1966; Whitaker, 1968).

The intensity data were collected on double-film equi-inclination Weissenberg photographs taken about the a and b axes with filtered copper radiation. The precautions necessary to obtain highly accurate measurements (Jeffery & Whitaker, 1965) were carried out. In this way the intensities of 568 independent reflexions were measured. Those reflexions too weak to measure (another 17) were given half the intensity of the weakest measurable reflexions and all reflexions were processed.

The observed intensities were corrected for absorption (linear absorption coefficient = 38 cm^{-1}) and Lorentz polarization factors. The two sets of photographs were correlated by the method of Rollett & Sparks (1960) and the scale factor and average temperature factor were obtained from Wilson's (1942) method.

Determination of the structure

The space group $Pmn2_1$ has fourfold general equivalent positions and twofold special equivalent positions, however there are only two molecules in the unit cell. If it is assumed that the phosphate group is tetrahedral and the water molecules are octahedrally arranged about the magnesium atom as in other magnesium salt hexahydrates, then the magnesium, phosphorus, nitrogen and two oxygen atoms of the phosphate group must lie on the mirror plane. Depending on the orientation of the water octahedron either two or four water molecules must also lie on the mirror plane and all other oxygen atoms (or water molecules) must be at least 1·2 Å away from it. These restrictions imposed by the space group were used in interpreting the Patterson synthesis.

Initial attempts to solve the structure from the a- and b-axis Patterson projections failed. The b-axis projection is similar to that reported by Bland & Basinski (1959), but the partial structure they postulated from this projection did not account for the a-axis projection. The number of peaks in these projections is considerably less than the theoretical number and the amount of superposition must be considerable. Because of this no further attempt was made to solve these projections.

The structure was finally solved from a three-dimensional Patterson synthesis in which the sharpening was obtained by multiplying the observed intensities by a function

$$c\left(k+\frac{\sin^2\theta}{\lambda^2}\right)\frac{1}{f^2}\exp\left(-\frac{\beta\sin^2\theta}{\lambda^2}\right).$$

k, the proportion of the sharpened Patterson series to be added to the gradient Patterson series, was taken as $\frac{1}{6}$ (Jacobson, Wunderlich & Lipscomb, 1961).

Table 1. *Coordinates for the structures obtained from the sharpened Patterson synthesis*

	S1			S2		
	x	y	z	x	y	z
P	0	0	0	0	0	0
O(1)	0	0	0·87	0	0	0·87
O(2)	0	0·80	0·05	0	0·20	0·05
O(3)	±0·18	0·12	0·05	±0·18	0·88	0·05
Mg	0	0·38	0·37	0	0·38	0·37
O(W1)	0	0·64	0·28	0	0·64	0·28
O(W2)	0	0·10	0·46	0	0·10	0·46
O(W3)	±0·22	0·25	0·25	±0·22	0·25	0·25
O(W4)	±0·22	0·50	0·50	±0·22	0·50	0·50
N	0	0·37	0·73	0	0·60	0·73

O(W1), O(W2) *etc.* are the oxygen atoms of the water molecules.

From this sharpened synthesis two possible structures (excluding the nitrogen atom) were obtained. The positions of the nitrogen atoms in the two structures were obtained from partially phased electron density sections at $x=0$. These structures were designated S1 and S2 and the atomic coordinates are given in Table 1. As the shortest oxygen–water distances are 2·71 and 2·40 Å for S1 and S2 respectively, the former structure would appear to be the more promising. However, the latter structure was not rejected as a similar short oxygen–water distance of 2·42 Å has been found elsewhere (Pedrazuela, García-Blanco & Rivoir, 1953).

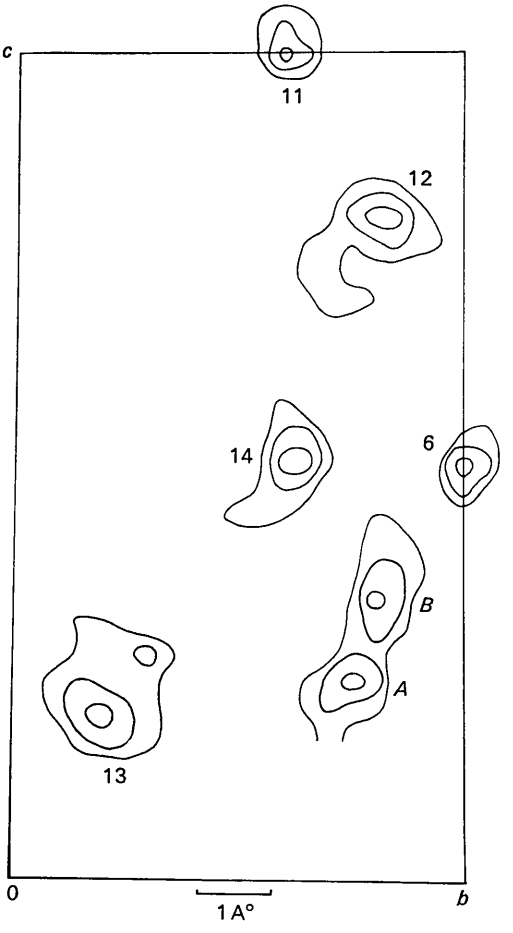

Fig. 1. Difference Fourier synthesis, sections calculated at various heights through the hydrogen atoms. (The heights are given in 60ths of the unit-cell edge.)

The residuals from (*a*) the initial data and (*b*) after a single cycle of least-squares refinement (Diamand, 1964) using individual isotropic temperature factors were

	(*a*)	(*b*)
S1	22·9%	15·3%
S2	32·4%	41·7%

In addition the output for the second crystal structure recommended negative temperature factors for some atoms. Because of this and the increased value of the residual the refinement of this structure was discontinued.

Refinement of the structure

The atomic scattering factors used were those given in *International Tables for X-ray Crystallography* (1962) for Mg^{2+} and neutral P,N and O. At a later stage in the refinement, modulus dispersion corrections were applied to the Mg^{2+} and P (*International Tables for X-ray Crystallography*, 1962).

Four additional cycles of least-squares refinement with individual isotropic temperature factors were carried out, at which stage the residual was hardly varying at 6·2%. Further refinement was carried out with individual anisotropic temperature factors until the residual remained stationary at 3·9%.

Three-dimensional difference Fourier syntheses were calculated at the end of both refinements. This was in case the atomic vibrations tended to mask the positions of the hydrogen atoms when isotropic temperature factors were used, or to absorb the hydrogen peaks in the case of anisotropic refinement. In fact, the two syntheses were very similar, the isotropic refinement producing some additional peaks due to the anisotropic vibrations of the heavier atoms. Attention was therefore confined to the anisotropic refinement synthesis.

It was found that the largest peaks on the difference electron density map were not due to the individual hydrogen atoms connected with the water molecules

Table 2. *Hydrogen positions, hydrogen bond lengths and bonded atoms*

The number or letter refers to the appropriate atom in Fig. 1.

	Number or letter	x	y	z	Bond length	Bonded atoms
H(1)	—	0·00	0·25	0·77	2·80	N, O(1)
H(2)	*A*	0·00	0·71	0·22	2·66	O(*W*1), O(2)
H(3)	*B*	0·00	0·82	0·32	3·15	O(*W*1), O(*W*2)
H(4)	6	0·12	0·02	0·49	2·65	O(*W*2), O(3)
H(5)	13	0·21	0·20	0·19	2·64	O(*W*3), O(3)
H(6)	12	0·20	0·81	0·79	2·69	O(*W*3), O(1)
H(7)	14	0·23	0·61	0·50	2·64	O(*W*4), O(3)
H(8)	11	0·18	0·59	0·00	2·63	O(*W*5), O(2)

but lay in a more or less continuous shell of electron density around the nitrogen atom. For reasons given in Whitaker & Jeffery (1970) it was concluded that the ammonium ion was bonded to one oxygen atom and the ion rotated about this bond as axis.

A scattering factor of this form would be very complicated to calculate and an approximate model was used of a randomly rotating ammonium group superimposed on which was a hydrogen atom corresponding to the bonding atom.

Detection of the hydrogen atoms in the water molecules

Fig. 1 and Table 2 give the positions of the hydrogen peaks (other than in NH_4^+) projected on to the mirror plane. Atoms *A* and *B* are on the mirror plane while the heights of the others are given in 1/60ths of the cell edge. The contours are at intervals of 0·1 e.Å^{-3} and the lowest contour is 0·1 e.Å^{-3}. The heights of the peaks were in the range 0·32 to 0·36 e.Å^{-3}.

Spurious peaks were obtained of maximum height 0·30 e.Å^{-3} but much sharper, and measurements of the electronic charge associated with several of the largest of these peaks gave values one-half or less than the electronic charge associated with a hydrogen peak. The hydrogen bond lengths given in Table 2 are further evidence of the correctness of this interpretation of the difference Fourier synthesis.

The bonded hydrogen atom H(1) of the ammonium group is also included in this Table for the sake of completeness.

It can be seen that all the hydrogen atoms except the one designated *B* take part in the bonding of the structure. If *B* also takes part in the bonding then this bond is considerably weaker than the others.

Final refinement of the structure including hydrogen atoms introduction

The final refinement of the structure took place in three parts. In the first the hydrogen atoms, with the exception of H(1), were included with isotropic temperature factors, the other atoms being included with anisotropic temperature factors and an attempt was made to refine the position and temperature factors simultaneously.

In the second part the first was repeated except that the hydrogen temperature factors were kept constant while in the third part the hydrogen atom H(1) was included and the refinement repeated again with constant temperature factors for the hydrogen atoms. The second part is not discussed here, but the effect of introducing H(1) is discussed in Whitaker & Jeffery (1970).

In all cases the refinement proved difficult because the hydrogen parameters tended to oscillate; this was

Table 3. *Parameters and standard deviations after refinement including hydrogen atom* H(1)

(*a*) Position parameters and isotropic temperature factors

	x	*y*	*z*	*B*
P	0·00000 (0)	−0·00661 (14)	−0·00052 (8)	—
O(1)	0·00000 (0)	−0·02221 (37)	0·86279 (20)	—
O(2)	0·00000 (0)	0·76229 (32)	0·05350 (21)	—
O(3)	0·18165 (22)	0·11371 (25)	0·04172 (15)	—
Mg	0·00000 (0)	0·37648 (19)	0·37185 (11)	—
O(*W*1)	0·00000 (0)	0·68219 (41)	0·28610 (22)	—
O(*W*2)	0·00000 (0)	0·08012 (42)	0·46451 (25)	—
O(*W*3)	0·21797 (24)	0·26377 (29)	0·26205 (14)	—
O(*W*4)	0·21055 (22)	0·48534 (28)	0·48494 (16)	—
NH_4	0·00000 (0)	0·36849 (50)	0·73063 (25)	—
H(1)	0·0000 (0)	0·3034 (75)	0·7507 (38)	4·00 (1·3)
H(2)	0·0000 (0)	0·7131 (73)	0·2222 (44)	4·00 (1·3)
H(3)	0·0000 (0)	0·7814 (78)	0·3150 (44)	4·00 (1·2)
H(4)	0·0989 (48)	0·0233 (45)	0·4947 (27)	4·00 (0·9)
H(5)	0·1883 (59)	0·1874 (59)	0·2059 (35)	4·00 (0·9)
H(6)	0·2242 (44)	0·8150 (65)	0·7930 (26)	4·00 (1·1)
H(7)	0·2348 (51)	0·5868 (60)	0·4994 (31)	4·00 (1·0)
H(8)	0·1846 (54)	0·5995 (55)	0·0026 (29)	4·00 (0·9)

(*b*) Anisotropic temperature factors ($\times 10^5$)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
P	788 (13)	749 (18)	243 (4)	−15 (21)	0 (0)	0 (0)
O(1)	1193 (48)	1343 (69)	226 (16)	−28 (62)	0 (0)	0 (0)
O(2)	1222 (52)	838 (66)	382 (17)	−22 (60)	0 (0)	0 (0)
O(3)	877 (30)	1152 (40)	375 (11)	−216 (41)	−32 (35)	−243 (72)
Mg	850 (20)	939 (29)	301 (7)	11 (28)	0 (0)	0 (0)
O(*W*1)	2966 (89)	1125 (78)	374 (21)	335 (63)	0 (0)	0 (0)
O(*W*2)	877 (54)	1819 (84)	950 (32)	1499 (72)	0 (0)	0 (0)
O(*W*3)	1237 (41)	1851 (54)	358 (14)	−260 (47)	−117 (39)	553 (80)
O(*W*4)	1272 (38)	1183 (44)	681 (16)	−512 (50)	−838 (43)	74 (76)
NH_4	1440 (70)	1068 (87)	371 (22)	638 (71)	0 (0)	0 (0)

attributed to interaction between the various parameters. The difficulties were overcome by applying half the shifts recommended by the least-squares program.

Refinement including hydrogen atom temperature factors

In the crystal structure determination of magnesium sulphate hexahydrate (Zalkin, Ruben & Templeton, 1964) the isotropic temperature factors for hydrogen were included in the refinement. The average final value obtained for the hydrogen temperature factors was 3·4 and this value was taken for the initial factor. The refinement proceeded until all shifts were less than one-tenth of the appropriate standard deviation (Mason, 1964). At this stage the hydrogen temperature factors varied from 0·09 to 8·69 and the average, 2·56, was approximately the same as the average for oxygen atoms of the water molecules, 2·55, obtained before. These effects are believed to be due to the experimental errors being large compared with the effects of varying the hydrogen temperature factors. Consequently these factors become absurd in attempting to minimize the effect of the errors. The residual and weighted residual (Hamilton, 1965) at this stage were 2·95% and 2·45% respectively.

Re-examination of the results of Zalkin, Ruben & Templeton (1964) indicates that the thermal param-

Table 4. *Observed and calculated structure factors*

H / L	K / $100\lvert F_o\rvert$	$100\lvert F_c\rvert$
• 0	0	
2	4334	5243
4	7766	8657
6	2407	2458
8	3739	3636
10	2052	2060
12	392	373
14	611	800
• 0	1	
0	1375	1454
1	2550	2477
2	4146	4202
3	1113	1112
4	1765	1752
5	662	642
6	1768	1716
7	867	875
8	734	765
9	2024	2042
10	752	770
11	804	774
12	683	679
13	554	562
14	437	532
• 0	2	
0	2123	2144
1	2355	2374
2	7044	7652
3	578	565
4	2435	2447
5	3356	3343
6	4251	4366
7	1304	1375
8	2714	2665
9	196	134
10	1516	1513
11	1045	1023
12	811	802
13	438	401
• 0	3	
0	2554	2669
1	305	341
2	3143	3263
3	4628	4574
4	370	447
5	246	206
6	733	700
7	2610	2631
8	2167	2132
9	1257	1272
10	925	923
11	854	865
12	628	645
13	854	830
• 0	4	
0	1604	1606
1	128	113
2	1223	1218
3	994	1007
4	2653	2706
5	637	589
6	2181	2161
7	534	526
8	1063	1120
9	583	624
10	1083	1096
11	419	411
12	1512	1535
• 0	5	
0	355	184
1	1600	1566
2	851	845
3	2059	2070
4	1088	1115
5	1203	1229
6	1409	1431
7	569	601
8	1476	1489
9	148	113
10	683	667
• 0	6	
0	808	802
1	1389	1410
2	1055	1039
3	615	601
4	937	909
5	1555	1589
6	1545	1561
7	524	571
8	1130	1177
9	74	163
• 0	7	
0	267	108
1	726	707
2	412	428
3	946	965
4	870	841
5	406	402
6	544	579
• 1	0	
1	2657	2827
3	4585	4664
5	2257	2202
7	1810	1763
9	1010	995
11	1479	1451
13	870	832
• 1	1	
0	1503	1471
1	4865	4847
2	1060	1054
3	744	734
4	1811	1802
5	3343	3287
6	1101	1153
7	2593	2647
8	1623	1598
9	2097	2092
10	413	365
11	474	375
12	166	175
13	346	357
14	406	484
• 1	2	
0	854	665
1	2347	2257
2	2276	2232
3	801	730
4	2167	2136
5	1546	1564
6	2097	2113
7	1656	1622
8	1310	1043
9	1736	1847
10	474	410
11	706	682
12	145	96
13	1033	1062
• 1	3	
0	3521	3281
1	982	1017
2	1347	1356
3	2371	2345
4	592	595
5	1323	1373
6	1159	1112
7	2216	2218
8	267	136
9	755	746
10	667	658
11	1600	1552
12	673	872
13	669	903
• 1	4	
0	323	308
1	2768	2732
2	948	940
3	1365	1372
4	513	548
5	1628	1607
6	378	381
7	1687	1684
8	611	616
9	1616	1531
10	569	518
11	569	563
12	222	265
• 1	5	
0	1283	1365
1	1351	1373
2	450	505
3	1617	1590
4	737	738
5	1350	1364
6	1611	1609
7	876	885
8	554	576
9	976	612
10	234	233
• 1	6	
0	267	169
1	841	863
2	1237	1251
3	954	1009
4	718	757
5	667	680
6	432	467
7	1312	1330
8	166	305
• 1	7	
0	1116	1144
1	1302	1329
2	748	727
3	889	861
4	246	178
5	691	740
6	296	333
• 2	0	
0	3889	3321
2	3064	2961
4	2523	2453
6	2451	2473
8	1622	1600
10	1071	1150
12	339	330
• 2	1	
0	3256	3234
1	5134	5102
2	5028	5226
3	3178	3195
4	3413	3429
5	4214	4184
6	3518	3553
7	1005	966
8	2011	2036
9	794	791
10	1343	1344
11	766	778
12	1474	1394
13	637	619
• 2	2	
0	1444	1504
1	1843	1754
2	2126	2002
3	3730	3710
4	801	770
5	2030	2060
6	419	387
7	787	754
8	2211	2196
9	826	840
10	457	395
11	385	341
12	1374	1382
13	399	402
• 2	3	
0	5657	5842
1	2853	2884
2	2758	2300
3	536	861
4	1541	1547
5	370	362
6	2088	2137
7	618	812
8	2071	2089
9	1103	1067
10	1164	1170
11	1021	961
12	128	18
• 2	4	
0	319	392
1	1203	1196
2	3013	2996
3	1393	1399
4	1365	1351
5	331	335
6	1468	1477
7	855	842
8	977	938
9	267	258
10	1059	1035
11	128	114
• 2	5	
0	3186	3169
1	363	382
2	1313	1267
3	488	524
4	351	594
5	181	45
6	1613	1623
7	486	423
8	1703	1664
9	693	682
10	432	373
• 2	6	
0	985	966
1	1335	1315
2	413	349
3	815	840
4	963	918
5	385	320
6	437	423
7	460	519
8	974	1044
• 2	7	
0	314	209
1	691	702
2	1039	1057
3	196	122
4	744	764
5	633	655
• 3	0	
1	867	872
3	2677	2748
5	2249	2277
7	1787	1805
9	1270	1270
11	1819	1804
13	1609	1588
• 3	1	
0	2074	2059
1	1291	1285
2	1707	1662
3	2739	2700
4	3173	3222
5	1304	1324
6	641	678
7	1776	1792
8	1759	1799
9	1943	1955
10	491	458
11	412	404
12	196	201
13	1126	1197
• 3	2	
0	2714	2744
1	1891	1916
2	693	694
3	1794	1758
4	1459	1461
5	1976	1975
6	3126	3060
7	2570	2542
8	748	737
9	1753	1768
10	733	721
11	1295	1227
12	679	711
• 3	3	
0	1568	1604
1	910	896
2	1626	1656
3	1782	1797
4	462	408
5	901	883
6	870	903
7	1215	1211
8	588	589
9	277	248
10	818	827
11	996	997
12	209	203
• 3	4	
0	432	430
1	4424	4425
2	658	675
3	1453	1456
4	766	752
5	2150	2149
6	246	166
7	1843	1810
8	533	523
9	1446	1422
10	128	182
11	597	647
• 3	5	
0	1455	1469
1	1407	1435
2	508	511
3	1771	1753
4	181	217
5	1241	1263
6	811	829
7	267	361
8	1013	970
9	413	421
• 3	6	
0	1190	1178
1	1461	1405
2	234	383
3	1459	1469
4	305	193
5	809	802
6	615	638
7	1449	1438
• 3	7	
0	480	485
1	787	787
2	876	853
3	592	548
4	399	415
• 4	0	
0	7737	7870
2	2629	2653
4	2020	2032
6	1081	1073
8	2519	2567
10	1415	1460
12	105	71
• 4	1	
0	399	310
1	1934	1963
2	1702	1711
3	246	59
4	928	945
5	844	803
6	1374	1397
7	307	306
8	480	491
9	838	836
10	773	773
11	825	611
12	883	925
• 4	2	
0	1036	1171
1	209	137
2	3044	2938
3	1705	1662
4	1248	1283
5	1268	1272
6	2286	2266
7	675	668
8	1713	1700
9	654	685
10	977	998
11	399	393
12	534	566
• 4	3	
0	2747	2771
1	1058	1056
2	1088	1114
3	1759	1792
4	606	573
5	592	560
6	1106	1150
7	1078	1063
8	1602	1599
9	554	552
10	574	572
11	412	449
• 4	4	
0	1405	1409
1	385	332
2	1636	1686
3	460	443
4	1991	1990
5	267	171
6	963	985
7	323	307
8	392	412
9	363	345
10	355	373
• 4	5	
0	1180	1180
1	628	606
2	892	896
3	1007	990
4	331	347
5	780	744
6	1419	1417
7	181	173
8	999	1023
• 4	6	
0	683	726
1	683	706
2	706	697
3	821	823
4	633	624
5	755	787
6	1013	975
• 5	0	
1	1890	1930
3	2114	2158
5	1756	1777
7	755	660
9	1252	1271
11	828	902
• 5	1	
0	1776	1775
1	3476	3336
2	801	808
3	1106	1144
4	450	422
5	2004	2008
6	671	652
7	1979	1962
8	1013	978
9	1509	1473
10	569	517
11	370	342
• 5	2	
0	457	439
1	1169	1184
2	1487	1494
3	615	695
4	1159	1169
5	815	821
6	752	764
7	951	949
8	1339	1335
9	1157	1161
10	457	449
11	438	475
• 5	3	
0	1409	1479
1	1083	1067
2	1384	1402
3	1844	1824
4	462	413
5	1458	1463
6	1007	1015
7	1710	1701
8	392	315
9	892	833
10	314	327
• 5	4	
0	181	48
1	1101	1066
2	363	309
3	1233	1202
4	196	125
5	1068	1068
6	497	446
7	1199	1150
8	419	430
9	889	889
• 5	5	
0	588	581
1	1026	1018
2	438	414
3	1199	1210
4	662	649
5	1624	1600
6	1176	1163
7	954	940
• 5	6	
0	355	298
1	544	523
2	982	967
3	347	342
4	907	863
• 6	0	
0	3960	3944
2	2035	2082
4	999	1010
6	1907	1944
8	1111	1123
10	355	369
• 6	1	
0	1548	1555
1	615	558
2	2054	2012
3	1045	1039
4	1432	1435
5	759	759
6	1071	1076
7	502	449
8	323	295
9	406	413
10	246	241
• 6	2	
0	1259	1306
1	695	679
2	1013	964
3	513	486
4	828	839
5	1405	1399
6	991	973
7	703	717
8	1255	1243
9	105	134
• 6	3	
0	1592	1604
1	857	620
2	1060	1076
3	1123	1131
4	432	374
5	419	360
6	848	830
7	628	635
8	1244	1254
• 6	4	
0	148	191
1	246	219
2	937	836
3	592	560
4	671	662
5	181	136
6	946	933
7	432	451
• 6	5	
0	988	972
1	462	445
2	626	620
3	706	728
4	234	226
• 7	0	
1	968	1007
3	1799	1750
5	1393	1393
7	675	694
• 7	1	
0	331	256
1	773	718
2	569	535
3	468	438
4	982	956
5	904	924
6	462	493
7	351	972
8	486	537
• 7	2	
0	620	582
1	1093	1053
2	438	461
3	1135	1112
4	633	660
5	968	954
6	925	928
7	1393	1422
• 7	3	
0	996	968
1	287	222
2	549	509
3	759	729
4	128	119
5	574	523
5	534	538
• 7	4	
0	105	80
1	1903	1881
2	222	313
3	637	626
4	267	259
• 8	0	
0	1512	1469
2	951	942
4	287	303
6	425	523
• 8	1	
0	425	461
1	826	805
2	889	888
3	166	154
4	673	898
5	662	671
• 8	2	
0	646	599
1	466	445
2	606	608
3	1010	1010
4	450	441
• 8	3	
0	1628	1556
1	706	685
2	809	784

eters for hydrogen also differed over a considerable range (1·3 to 5·9 Å^2) although not as large as in the present investigation. The present refinement was discontinued when the parameter shifts were less than one-tenth the standard deviation. Had the refinement been discontinued at an earlier stage, say one-third the standard deviation, the range of hydrogen thermal parameters would be smaller. This may be the reason for the smaller range of parameters obtained by Zalkin, Ruben & Templeton. However, they do not give a criterion for ending the refinement.

Refinement with constant hydrogen temperature factors

It has already been mentioned that Zalkin, Ruben & Templeton (1964) found an average isotropic temperature factor for hydrogen of 3·4. In view of this and Baur's (1964*a*) suggestion that an isotropic temperature factor for hydrogen should be 1·3 plus the temperature factor for the oxygen atom in the same water molecule, it was decided that a constant isotropic temperature factor of 4·0 should be used for the hydrogen atoms. However, as a check on the effect of these temperature factors the calculations were repeated using a temperature factor of 3·0.

Refinement including the hydrogen atom H(1)

The final position and temperature parameters are given in Table 3 for the case of a hydrogen temperature factor of 4·0. Compared with the parameters in this Table, when the hydrogen temperature factor is 3·0 the maximum positional parameter difference was $0{\cdot}7\sigma$ and the maximum temperature parameter difference was $0{\cdot}4\sigma$, thus indicating a negligible effect of a difference of 1·0 in the hydrogen temperature factor. The same effect is obtained when the hydrogen atom H(1) is excluded from the refinement. Thus it would appear that, in the present case, a difference in the hydrogen temperature factors comparable with the standard deviation does not have a significant effect on the remainder of the structure.

The residual, weighted residual and standard deviation of electron density for the parameters given in Table 3 were 2·84%, 2·34% and 0·125 e.Å^{-3} respectively, while when the hydrogen temperature factor was 3·0 these were 2·82%, 2·30% and 0·126 e.Å^{-3}. These results for the residual and weighted residual are marginally better than those obtained when a hydrogen temperature factor of 4·0 is used and the same effect was found when the refinement excluded the hydrogen atom H(1). This improvement would be expected in view of the low average hydrogen temperature factor already mentioned. In spite of the improvement of residual and weighted residual caused by having a hydrogen temperature factor of 3·0, it is thought that the higher value of 4·0 is probably more realistic and the parameters given in Table 3 are used for the remainder of the discussion.

A composite electron density map of the asymmetric unit is given in Fig. 2 and the Table of observed and calculated structure factors in Table 4. An examination of this Table gives no reason to believe that extinction is present.

Discussion of the structure

General

The structure obtained for struvite is essentially that given by González & de Lerma (1955) and González & García-Blanco (1955) for magnesium ammonium arsenate hexahydrate.

The structure consists of PO_4 tetrahedra, $Mg.6H_2O$ octahedra and ammonium groups, held together by hydrogen bonds. These bonds are predominantly electrostatic in character (Moeller, 1952; Smith, 1955) and so the bonding may also be thought of as ionic. The *a*-axis projection of the unit cell is given (Fig. 3), with

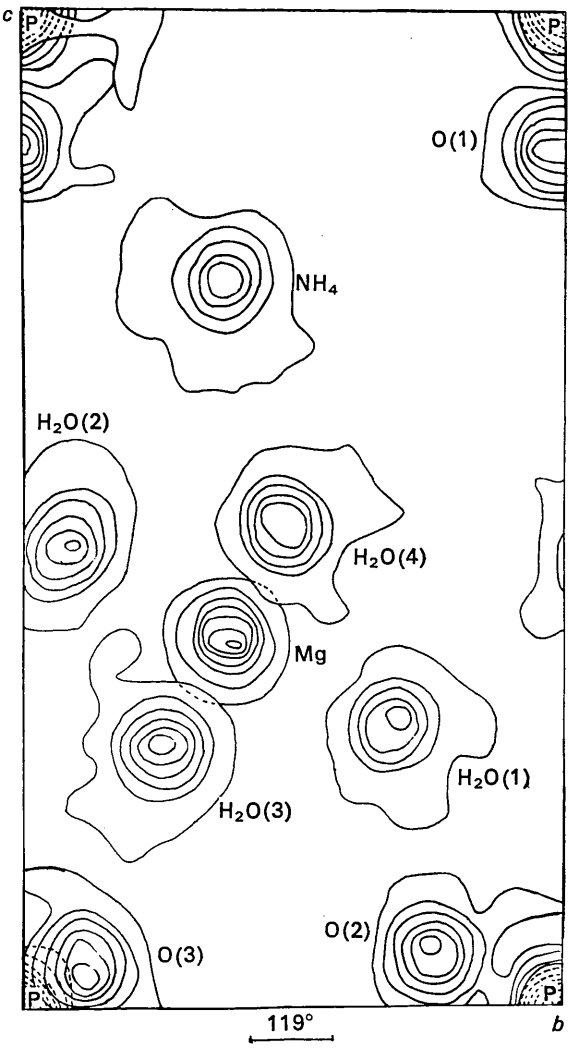

Fig. 2. A composite electron density map of the asymmetric unit calculated on sections through the atom peaks. The contouring is at intervals of 5 e.Å^{-3} around the phosphorus and magnesium atoms and 2 e.Å^{-3} about the other atoms. First contour zero.

those atomic groupings associated with the mirror plane at $x=0$ drawn with bold lines. It can be seen that the structure is in layers perpendicular to the c axis. These layers are held together by two hydrogen bonds per unit cell. This no doubt accounts for the good (001) cleavage mentioned by Palache *et al.* (1944). The other cleavage mentioned by Palache *et al.* (1944), (010), requires the breaking of eight or nine hydrogen bonds (depending on whether H(3) takes part in the bonding or not) and the cleavage would have to be stepped.

Bond lengths and angles uncorrected for thermal vibration

PHOSPHATE TETRAHEDRON

The individual values of the phosphorus–oxygen and oxygen–oxygen distances are given in Table 5. The weighted mean values are:

phosphorus–oxygen	$1{\cdot}5370 \pm 0{\cdot}0011$ Å
oxygen–oxygen	$2{\cdot}5098 \pm 0{\cdot}0014$ Å

The mean value obtained for the phosphorus–oxygen bond is in agreement with the results of other accurate investigations (Table 6). In this Table the errors in the means are not all given by the authors; some have been calculated from variations in the individual results.

Examination of O–P–O angles in Table 5 indicates that the tetrahedron is almost regular, there being no significant variation in the bond lengths and all angles being within 1° of that for a regular tetrahedron. The differences from the theoretical angle are apparently statistically significant ($>3\sigma$), but in view of the lack of knowledge of the effect of thermal vibrations on

Table 5. *Bond lengths and angles*

Phosphate tetrahedron

	Distance		Distance		Angle
P–O(1)	1·5338 (24) Å	O(1)–O(2)	2·5121 (32) Å	O(1)–P–O(2)	109·52 (13)°
P–O(2)	1·5419 (22)	O(1)–O(3)	2·5102 (25)	O(1)–P–O(3)	109·72 (8)
P–O(3)	1·5358 (16)	O(2)–O(3)	2·5017 (23)	O(2)–P–O(3)	108·75 (8)
Mean	1·5370 (11)	O(3)–O(3*a*)	2·5217 (31)	O(3)–P–O(3*a*)	110·36 (14)
		Mean	2·5098 (14)		

$Mg.6(H_2O)$ octahedron

	Distance		Distance		Angle
Mg–O(*W*1)	2·1076 (27) Å	O(*W*1)–O(*W*3)	2·9925 (28) Å	O(*W*1)–Mg–O(*W*3)	91·54 (8)°
Mg–O(*W*2)	2·0940 (29)	O(*W*1)–O(*W*4)	2·9247 (27)	O(*W*1)–Mg–O(*W*4)	89·51 (8)
Mg–O(*W*3)	2·0687 (18)	O(*W*2)–O(*W*3)	2·9496 (28)	O(*W*2)–Mg–O(*W*3)	90·24 (8)
Mg–O(*W*4)	2·0460 (19)	O(*W*2)–O(*W*4)	2·8935 (28)	O(*W*2)–Mg–O(*W*4)	88·67 (8)
Mean	2·0711 (11)	O(*W*3)–O(*W*3*a*)	3·0259 (32)	O(*W*3)–Mg–O(*W*3*a*)	94·00 (11)
		O(*W*3)–O(*W*4)	2·8430 (24)	O(*W*4)–Mg–O(*W*4*a*)	91·17 (11)
		O(*W*4)–O(*W*4*a*)	2·9229 (31)		
		Mean	2·9284 (11)		

Table 6. *Comparison of observed bond lengths*

Phosphorus–oxygen

Reference	Compound	P–O
Geller & Durand (1960)	$LiMnPO_4$	1·541 (5) Å
Iitaka & Huse (1965)	$C_{10}H_{26}N_4.2H_3PO_4.6H_2O$	1·538 (3)
Li & Caughlan (1965)	$Ca(C_{10}H_2HPO_4)_2.3H_2O$	1·535 (3)
Cid-Dresdner (1966)	Turquois	1·540 (2)
Fanfani & Zanazzi (1967)	$Fe_{0.5}^{II}Fe_{2.5}^{III}(OH)_{2.5}(PO_4)_3.H_2O$	1·535 (3)
Greenblatt, Banks & Post (1967)	Ca_2PO_4Cl	1·541 (1)
Sutor (1967)	$MgHPO_4.3H_2O$	1·544 (2)
This work	$MgNH_4PO_4.6H_2O$	1·537 (1)

Magnesium–oxygen

Reference	Compound	Mg–O
Margulis & Templeton (1962)	$Mg(NH_4)_2(SO_4)_2.6H_2O$	2·064 (3) Å
Nardelli, Fava & Giraldi (1962)	$MgS_2O_3.6H_2O$	2·083 (6)
Zalkin, Ruben & Templeton (1964)	$MgSO_4.6H_2O$	2·066 (1)
Baur (1964*a*)	$MgSO_4.7H_2O$	2·065 (2)
*Baur (1964*b*)	$MgSO_4.4H_2O$	2·077 (2)
Johnson (1965)	$[Mg(H_2O)_6][MgC_6H_5O_7H_2O]_2.2H_2O$	2·074 (1)
Sasvari & Jeffery (1966)	$MgCl_2.12H_2O$	2·062 (4)
This work	$MgNH_4PO_4.6H_2O$	2·071 (1)

* Neutron diffraction study.

these angles (Busing & Levy, 1964), it would be unwise to say that the tetrahedron is not regular.

Each oxygen atom is bonded to four other atoms, one phosphorus and three hydrogen atoms (Fig. 4). The bonding atoms are at the corners of a distorted tetrahedron, the average oxygen–hydrogen bond length being 1·93 Å compared with 1·537 Å obtained for the average phosphorus–oxygen distance. In addition the angles of this tetrahedron are distorted, the averages being 117° for ∠P–O–H and 101° for ∠H–O–H. However, the ranges of these angles are considerably greater than the standard deviations, being $112 \pm 1°$ to $128 \pm 1°$ for ∠P–O–H and $90 \pm 1{\cdot}5°$ to $112 \pm 1{\cdot}5°$ for ∠H–O–H. Even though these standard deviations are almost certainly too low in the sense that they ignore the thermal vibrations (Busing & Levy, 1964), the angular differences are probably significant.

If the distortion of the phosphate tetrahedron is, in fact, significant then it may be caused by the distortion in the tetrahedron around the oxygen atom. It is interesting to note that the oxygen atom O(3) which is involved in both O–P–O angles and both O–O distances which are significantly different from the mean values is also the centre of the most distorted tetrahedron.

$Mg.6H_2O$ OCTAHEDRON

The individual values of the magnesium–oxygen and oxygen–oxygen distances are given in Table 5. The weighted mean values are:

magnesium–oxygen	$2{\cdot}0711 \pm 0{\cdot}0011$ Å
oxygen–oxygen	$2{\cdot}9284 \pm 0{\cdot}0011$ Å

Detailed examination of the individual values indicates that the octahedron is very distorted, the range of magnesium–oxygen distances being 21σ, where σ is the largest standard deviation. In addition the 'right angles' vary considerably, one being as large as 94·00° and the difference between this and the regular value corresponds to 36σ. Some of this distortion may be due to thermal vibration but it is thought that, because equivalent values vary so much, the distortion must be due to other causes in addition. The average value for the magnesium–oxygen distance is compared with those obtained by other investigators (Table 6): the agreement is reasonable. It is interesting to note that some distortion of the $Mg.6H_2O$ octahedron occurs in every compound in this Table.

Three of the water oxygen atoms, O(W1), O(W3) and O(W4) are each bonded to three atoms (the magnesium and two hydrogen atoms). However, the water oxygen atom O(W2) may have another bond. In addition to the three already mentioned, it may be an acceptor atom for a hydrogen bond from the water oxygen atom O(W1). If there is a fourth bond to the water oxygen atom O(W2) it would seem reasonable to expect it to distort the configuration of the other bonds.

Consider now the sum of the angles Mg–O(W)–H_a, Mg–O(W)–H_b and H_a–O(W)–H_b. For atoms O(W1) and O(W4), it is $360 \pm 8°$ and $357 \pm 7°$ respectively, *i.e.* the magnesium, oxygen and two hydrogen atoms are approximately coplanar. These values are similar to the average value of 354° found by Baur (1964*b*) in the case of magnesium sulphate tetrahydrate. For atom O(W2) the sum is $357 \pm 5°$ and this would seem to suggest that the inter-water hydrogen bonding is too weak to affect the atomic configuration. Because of this it would seem reasonable to conclude that there is probably no inter-water hydrogen bonding. The bonding this assumption is shown schematically in Fig. 4.

In the case of the water oxygen atom O(W3) the sum of the angles is $325 \pm 5°$ and thus is considerably less than for the other atoms.

It is interesting to note that if one considers the oxygen atoms about each water oxygen atom, then the sums of the angles subtended by these and the magnesium atom are 360°, 360°, 350° and 358° for O(W1), O(W2), O(W3) and O(W4) respectively and the agreement is much better. This is because the hydrogen atoms associated with O(W3) are in bonds which are not collinear. This is dealt with later.

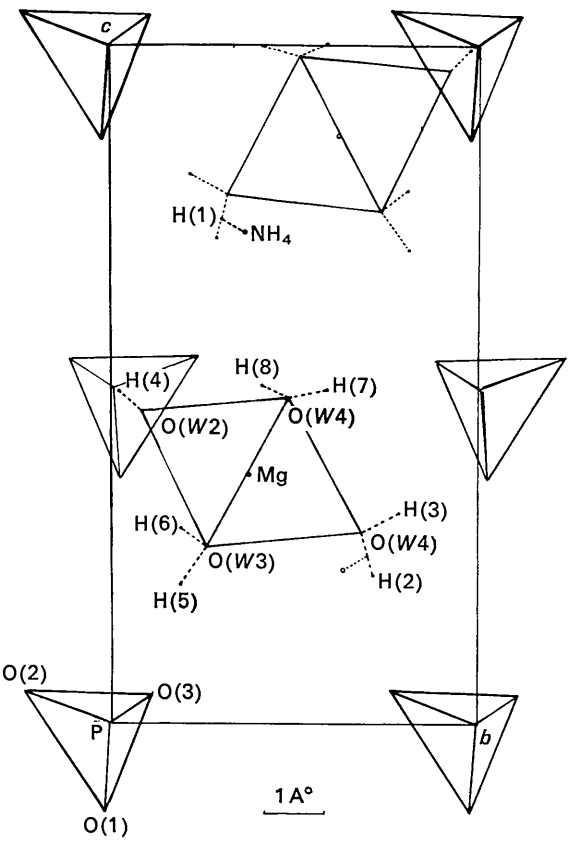

Fig. 3. The *a*-axis projection, with those groupings associated with the mirror plane at $x = 0$, drawn with bold lines. Atoms P, O(1), O(2), Mg, O(W1), O(W2), NH_4^+, H(1), H(2) and H(3) are on this plane; all other atoms are in vertical pairs.

In the case of magnesium sulphate heptahydrate Baur (1964*a*) found that the average magnesium–oxygen bond length was 2·096 Å when the oxygen atom was an acceptor atom for a hydrogen bond. On the other hand, in the cases of the oxygen atom not being an acceptor for a hydrogen bond, the average magnesium–oxygen bond length was 2·050 Å. He suggests that for acceptor atoms the sum of the electrostatic bonds is increased and the magnesium–oxygen distance lengthens to achieve electrostatic balance.

In the case of struvite two long magnesium–oxygen bonds are obtained, the longest of which is longer than any of those found by Baur (1964*a*). What is more, there is no inter-water hydrogen bonding, and if there were, the longest magnesium–oxygen bond length would be associated with the donor atom of the hydrogen bond. Thus Baur's explanation (1964*a*) cannot apply to struvite and the fact that such long magnesium–oxygen bonds can be obtained in struvite must be due to some other cause. It is presumably due to the different environments of the water oxygen atoms.

González & García-Blanco (1955) found a very short magnesium–oxygen distance of 1·76 Å in magnesium ammonium arsenate hexahydrate. This anomalous distance is not found in the present determination and as the structures are isomorphous it is presumably due to experimental error.

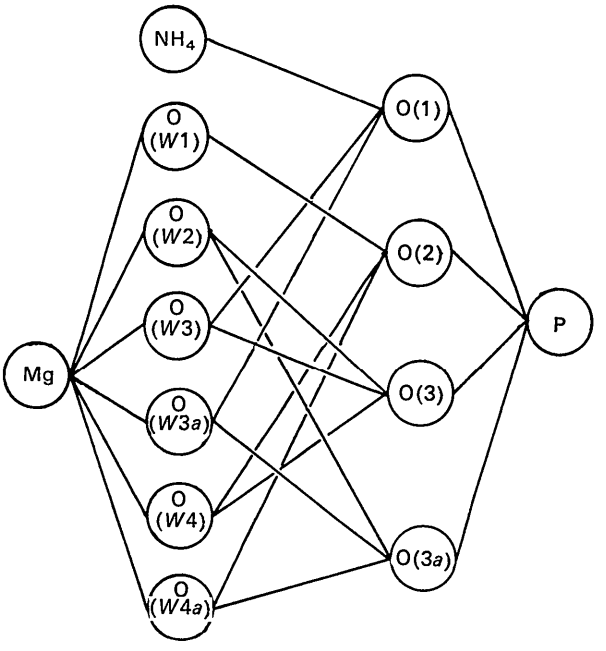

Fig. 4. Schematic diagram of proposed bonding.

Ammonium group

The evidence for a single-bonded ammonium group with the group rotating about this bond as axis is given in Whitaker & Jeffery (1970). The final interatomic distances are slightly different from those given in that paper, because of further refinement, but not significantly so. The final values are:

ammonium–oxygen	O(1)	2·818(4) Å
ammonium–water	O(*W*3)	3·008(3) Å
ammonium–water	O(*W*2)	3·466(4) Å
ammonium–water	O(*W*4)	3·197(3) Å

Although the first of these (the hydrogen bond) has lengthened slightly it is still less than the average hydrogen bond length in ammonium structures (Pimentel & McClellan, 1960) and the alteration does not invalidate anything in the paper by Whitaker & Jeffery (1970).

Hydrogen bonding

The distances and angles involved in the hydrogen bonding are given in Table 7. The weighted mean of the oxygen O(*W*)–hydrogen bond is 0·778 ± 0·014 Å. This is considerably less than the same distances obtained from neutron diffraction measurements (there would appear to be no X-ray results of comparable accuracy); Baur (1964*b*) gives 0·967(5) Å for this distance in magnesium sulphate tetrahydrate and Bacon & Curry (1962) give 0·96 Å in copper sulphate pentahydrate. The discrepancy may be due to either or both of the following factors: (*a*) thermal vibrations of the atoms and (*b*) neutron diffraction and X-ray diffraction

Table 7. *Hydrogen bonding, distances and angles*

	Distances		Angle
	O(*W*)–H	O(*W*)–O	O(*W*)–H–O
H(2)	0·74 (5) Å	2·651 (3) Å	174 (5)°
H(3)	0·69 (5)	3·155 (4)	166 (5)
H(4)	0·84 (3)	2·654 (2)	173 (3)
H(5)	0·81 (4)	2·646 (2)	154 (4)
H(6)	0·71 (3)	2·702 (2)	163 (4)
H(7)	0·66 (4)	2·649 (2)	178 (4)
H(8)	0·92 (4)	2·633 (2)	173 (3)
	N–H	N–O	
*H(1)	0·46 (4)	2·818 (4)	177 (7)

	Angle
H(2)–O(*W*1)–H(3)	103 (5)°
H(4)–O(*W*2)–H(4*a*)	109 (4)
H(5)–O(*W*3)–H(6)	97 (4)
H(7)–O(*W*4)–H(8)	106 (4)

* Because of the superposition of a spherical distribution and a single atom, this bond length has very little significance and is not discussed further.

techniques not measuring the same distances. Neutron diffraction techniques measure the inter-nuclear distance while X-ray diffraction methods give the peak electron density positions.

In the X-ray diffraction investigation of ammonium bifluoride, McDonald (1960) found that the N–H bond length was $0{\cdot}88 \pm 0{\cdot}03$ Å compared with the inter-nuclear distance of $1{\cdot}025 \pm 0{\cdot}005$ Å found from nuclear magnetic resonance measurements from the same compound (Gutowsky, Kistiakowsky, Pake & Purcell, 1949). This gives a bond length to inter-nuclear distance ratio of $0{\cdot}86 \pm 0{\cdot}03$. Banyard & March (1961) theoretically investigated the radial electron density distribution of the ammonium group obtained from the self consistent wave calculations of Bernal & Massey (1954) and concluded that the electrons associated with the hydrogen atoms should be at a distance from the nitrogen nucleus of $0{\cdot}76 \pm 0{\cdot}06$ of the nuclear separation. In the present work it is found that for the oxygen–hydrogen distances the average bond length to inter-nuclear distance ratio is 0·81 which is comparable with the results for the ammonium group. Thus it would appear that the discrepancy between the present results and neutron diffraction measurements is due largely to measuring peak positions of electron density in the present investigation and inter-nuclear distances with neutron diffraction techniques.

The probable reason for the discrepancy between the results is that the single electron of the hydrogen atom is used in bond formation and is drawn towards the bonding atom, thus giving shorter bond lengths. This causes the hydrogen atom to become a dipole and so give the 'hydrogen bond' its predominantly electrostatic character (Moeller, 1952; Smith, 1955).

The angles H–O(*W*)–H do not differ significantly from the tetrahedral angle and, with the exception of H(5) and H(6), the atoms O(*W*)–H–O do not significantly differ from collinearity. Non-collinear hydrogen bonding has been found before in copper sulphate pentahydrate and in oxalic acid dihydrate (Bacon & Curry, 1962). In these compounds the minimum ∠O(*W*)–H–O values are 156 and 154° respectively. Hence the values obtained are not unreasonable. However, in these compounds mentioned the reason for non-collinearity was the need to accommodate the hydrogen atoms subtending a tetrahedral angle at the oxygen atom, while in the present case this is not so. If the atoms O(*W*)–H–O were collinear for H(5) and H(6) then ∠H(5)–O(*W*3)–H(6) would be 105° which is nearer to the tetrahedral value than that obtained (Table 7). There would appear to be no reason for this unless the errors are underestimated due to thermal vibration (Busing & Levy, 1964).

Analysis of thermal vibrations

The r.m.s. displacements and the direction cosines of the axes of the thermal vibration ellipsoids are given in Table 8. The errors in the displacements were obtained by calculating the vibration ellipsoids for the values in Table 3 plus the standard deviation, and minus the standard deviations and averaging over similar atoms.

Table 8. *R.m.s. displacements and orientation with respect to crystallographic axes*

	R.m.s. displacement	Direction cosine with respect to a	b	c
P	0·139 ± 1	1·000	0·000	0·000
	0·124 ± 1	0·000	−0·212	0·977
	0·119 ± 1	0·000	0·977	0·212
O(1)	0·171 ± 4	1·000	0·000	0·000
	0·160 ± 4	0·000	0·999	−0·043
	0·120 ± 4	0·000	0·043	0·999
O(2)	0·173 ± 4	1·000	0·000	0·000
	0·156 ± 4	0·000	−0·046	0·999
	0·126 ± 4	0·000	−0·999	−0·046
O(3)	0·164 ± 4	−0·224	0·654	−0·723
	0·151 ± 4	0·812	−0·286	−0·510
	0·132 ± 4	−0·540	−0·701	−0·467
Mg	0·144 ± 2	1·000	0·000	0·000
	0·138 ± 2	0·000	0·153	0·988
	0·134 ± 2	0·000	−0·988	0·153
O(*W*1)	0·269 ± 4	1·00	0·000	0·000
	0·169 ± 4	0·000	0·635	0·772
	0·129 ± 4	0·000	−0·772	0·635
O(*W*2)	0·277 ± 4	0·000	0·529	0·849
	0·146 ± 4	1·000	0·000	0·000
	0·136 ± 4	0·000	−0·849	0·529
O(*W*3)	0·202 ± 4	0·521	0·810	−0·271
	0·162 ± 4	0·852	−0·514	0·102
	0·146 ± 4	0·057	0·284	0·957
O(*W*4)	0·238 ± 4	0·534	0·226	−0·815
	0·157 ± 4	−0·644	0·733	−0·219
	0·126 ± 4	0·547	0·642	0·537
NH_4	0·187 ± 4	1·000	0·000	0·000
	0·182 ± 4	0·000	0·655	0·756
	0·104 ± 4	0·000	−0·756	0·655

In the case of the phosphorus and magnesium atoms it can be seen that the vibrations are approximately isotropic although in the case of phosphorus there is a significant distortion from a sphere, the shortest axis being 11° from the direction of O(3). For the phosphate oxygen atoms O(1), O(2) and O(3) it is found that the shortest axes of the vibration ellipsoids make angles of 1°, 21° and 22° with the respective phosphorus–oxygen bonds, while the longest axes make angles of 90°, 90° and 85° respectively. In the case of the water oxygen atoms, the vibration ellipsoids approximate to prolate spheres and the longest axes for O(*W*1), O(*W*2), O(*W*3) and O(*W*4) are at angles of 90°, 88°, 76° and 88° to the respective bonds, while the shortest ones are at angles of 12°, 6°, 51° and 21° respectively.

Finally, for the ammonium group the vibration ellipsoid is very nearly that of an oblate sphere and the unique axis is only 9° from the ammonium–oxygen O(1) bond. It is interesting to note that this is what would be expected from a singly-bonded ammonium group and would seem to contradict the electrostatic balance diagrams of González & García-Blanco (1955). These imply that the ammonium group is equally

bonded to the six nearest neighbours. It was thought that this thermal vibration ellipsoid might have been influenced by the introduction of the hydrogen atom H(1) as this lies on the NH_4–O(1) bond. Because of this the vibration ellipsoids were calculated for the structure without this hydrogen atom. However, the vibration ellipsoids are only very slightly changed and the same conclusions apply.

Bond lengths corrected for thermal vibrations

Busing & Levy (1964) have pointed out that one of the effects of thermal vibration is to alter the apparent bond lengths and showed how to correct for these effects. Corrected bond lengths have been calculated for the phosphorus–oxygen, magnesium–oxygen and oxygen–hydrogen bonds for three cases; (*A*) the atoms are vibrating in phase, (*B*) the lighter atoms are riding on the inner ones,* and (*C*) the atoms are moving independently of each other. The values are given in Table 9.

In the case of phosphorus–oxygen bond lengths, the shortest r.m.s. displacements of the oxygen atoms are almost along the bonds and the values of these displacements are approximately the same as for the phosphorus atom, while the largest displacements are perpendicular to the P–O bond. The riding-corrected value would therefore appear to be the best; thus

$$\text{phosphorus–oxygen} = 1{\cdot}5431 \pm 0{\cdot}0011 \text{ Å}.$$

In the case of the $Mg.6H_2O$ octahedron the shortest r.m.s. displacements of the oxygen atoms are along the bonds except for O(*W*3). However as the vibration ellipsoids approximate to prolate spheres this is probably not very significant, probably more important is that the longest axes are approximately perpendicular to the appropriate Mg–O bond. The value of the smallest displacement is approximately the same as that for the magnesium atom; thus again the riding model would appear to be the best but not as good as for the phosphate group. Thus

$$\text{magnesium–oxygen} = 2{\cdot}0810 \pm 0{\cdot}0011 \text{ Å}.$$

Margulis & Templeton (1962) and Baur (1964*b*) have all taken the riding model to be the best for the $Mg.6H_2O$ octahedron. The values obtained are 2·075 ± 0·003 and 2·081 ± 0·002 Å; the present values are in reasonable agreement. On the other hand, Zalkin, Ruben & Templeton (1964) have taken the thermal motion in this octahedron to be 'in-phase'. Values for both types of motion are given in the present case.

In the case of oxygen–hydrogen bonds, Busing & Levy (1964) suggest the riding model to be the best. This gives a bond length of 0·792 Å, which still gives a discrepancy of 0·17 Å compared with the values given by other investigators from neutron diffraction (Bacon & Curry, 1962; Baur, 1964*b*) but this corrected value assumes that the vibrations of the hydrogen atoms are isotropic and this is unlikely. Even so, it would be unlikely that the discrepancy between the X-ray and neutron diffraction results can be accounted for in this way. Hence it would appear that either oxygen–hydrogen bonds measured by X-ray diffraction techniques are somewhat shorter than those measured by neutron diffraction methods, or the oxygen–hydrogen bonds are unusually short in struvite (although there would appear to be no reason for this).

It would seem advisable to check these bonds, and the prediction of a single-bonded ammonium group, by neutron diffraction techniques and this is currently being done by one of us (A.W.).

This paper incorporates work submitted by one of us (A.W.) in part fulfilment of a Ph.D. thesis of the University of London. We should like to thank the Science Research Council for support and Professor J. D. Bernal for encouragement and for facilities for carrying out this work.

* In this case the vector separation is independent of the position of the ridden atom.

Table 9. *Bond lengths corrected for thermal vibrations*

	Uncorrected bond length	Corrected bond length *A*(in-phase)	*B*(riding)	*C*(independent)	Standard deviation
P–O(1)	1·5338 Å	1·5346 Å	1·5407 Å	1·5626 Å	0·0024
P–O(2)	1·5419	1·5425	1·5478	1·5701	0·0022
P–O(3)	1·5358	1·5364	1·5416	1·5619	0·0016
Mean	1·5370	1·5376	1·5431	1·5642	0·0011
Mg–O(*W*1)	2·1076	2·1109	2·1220	2·1409	0·0027
Mg–O(*W*2)	2·0940	2·0971	2·1079	2·1268	0·0029
Mg–O(*W*3)	2·0687	2·0694	2·0747	2·0930	0·0018
Mg–O(*W*4)	2·0460	2·0479	2·0563	2·0748	0·0019
Mean	2·0711	2·0730	2·0810	2·0996	0·0011
O(*W*1)–H(2)	0·740	0·740	0·743	0·874	0·049
O(*W*1)–H(3)	0·689	0·690	0·697	0·829	0·049
O(*W*2)–H(4)	0·841	0·841	0·845	0·958	0·032
O(*W*3)–H(5)	0·811	0·814	0·834	0·913	0·039
O(*W*3)–H(6)	0·718	0·721	0·746	0·830	0·035
O(*W*4)–H(7)	0·665	0·666	0·682	0·800	0·036
O(*W*4)–H(8)	0·917	0·918	0·932	1·011	0·036
Mean	0·778	0·780	0·792	0·895	0·014

References

BACON, G. E. & CURRY, N. A. (1962). *Proc. Roy. Soc.* A**266**, 95.
BANYARD, K. E. & MARCH, N. H. (1961). *Acta Cryst.* **14**, 357.
BAUR, W. H. (1964*a*). *Acta Cryst.* **17**, 1361.
BAUR, W. H. (1964*b*). *Acta Cryst.* **17**, 863.
BERNAL, M. J. M. & MASSEY, H. S. W. (1954). *Mon. Not. R. Astr. Soc.* **114**, 172.
BLAND, J. A. & BASINSKI, S. J. (1959). *Nature, Lond.* **183**. 1385.
BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142.
CID-DRESDNER, H. (1965). *Z. Kristallogr.* **121**, 87.
DIAMAND, R. D. (1964). Private communication.
FANFANI, L. & ZANAZZI, P. F. (1967). *Acta Cryst.* **22**, 173.
FARQUHAR, M. C. M. & LIPSON, H. (1946). *Proc. Phys. Soc.* **58**, 200.
GELLER, S. & DURAND, J. L. (1960). *Acta Cryst.* **13**, 325.
GONZÁLEZ, R. F. & GARCÍA-BLANCO, S. (1955). *An. Soc. esp. Fís. Quím.* A**51**, 29.
GONZÁLEZ, R. F. & DE LERMA, J. L. (1955). *An. Soc. esp. Fís. Quím.* A**51**, 19.
GREENBLATT, M., BANKS, E. & POST, B. (1967). *Acta Cryst.* **23**, 166.
GUTOWSKY, H. S., KISTIAKOWSKY, G. B., PAKE, G. E. & PURCELL, E. M. (1949). *J. Chem. Phys.* **17**, 972.
HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1949). *Research*, **2**, 338.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
IITAKA, Y. & HUSE, Y. (1965). *Acta Cryst.* **18**, 110.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JACOBSON, R. A., WUNDERLICH, J. A. & LIPSCOMB, W. N. (1961). *Acta Cryst.* **14**, 598.
JEFFERY, J. W. & WHITAKER, A. (1965). *Acta Cryst.* **19**, 963.
JOHNSON, C. K. (1965). *Acta Cryst.* **18**, 1004.
LI, C-T. & CAUGHLAN, C. N. (1965). *Acta Cryst.* **19**, 637.
LONSDALE, K. & SUTOR, D. J. (1966). *Science*, **154**, 1353.
MCDONALD, T. R. R. (1960). *Acta Cryst.* **13**, 113.
MARGULIS, T. N. & TEMPLETON, D. H. (1962). *Z. Kristallogr.* **117**, 344.
MASON, R. (1964). *Acta Cryst.* **17**, 547.
MELLOR, J. W. (1923). *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 4, p. 384. London: Longmans.
MOELLER, T. (1952). *Inorganic Chemistry*, p. 188. New York: Wiley; London: Chapman & Hall.
NARDELLI, M., FAVA, G. & GIRALDI, G. (1962). *Acta Cryst.* **15**, 227.
PALACHE, C., BERMAN, H. & FRONDEL, C. (1951). *Dana's System of Mineralogy*, Vol. II, p. 715.
PEDRAZUELA, A. R., GARCIA-BLANCO, S. & RIVOIR, L. (1953). *An. Soc. esp. Fís. Quím.* A**49**, 255.
PIMENTEL, G. C. & MCCLELLAN, A. L. (1960). *The Hydrogen Bond*, p. 289. San Francisco, London: Freeman.
ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.
SASVARI, K. & JEFFERY, G. A. (1966). *Acta Cryst.* **20**, 875.
SMITH, J. W. (1955). *Electric Dipole Moments*, p. 302. London: Butterworth.
Structure Reports for 1955 (1963). **19**, 440. Utrecht: Oosthoek.
SUTOR, D. J. (1967). *Acta Cryst.* **23**, 418.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.
WHITAKER, A. (1968). *Miner. Mag.* **36**, 820.
WHITAKER, A. & JEFFERY, J. W. (1970). *Acta Cryst.* B**26**, 1440.
ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1964). *Acta Cryst.* **17**, 235.

Acta Cryst. (1970). B**26**, 1440

X-ray Evidence for a Single-Bonded Rotating Ammonium Ion in Struvite

BY A. WHITAKER* AND J W. JEFFERY

Department of Crystallography, Birkbeck College, University of London, England

(*Received* 23 *June* 1969)

X-ray evidence is presented in favour of a single-bonded rotating ammonium ion in struvite at room temperature. The evidence consists of difference Fourier syntheses, bond lengths and the shape and orientation of the vibration ellipsoid.

Introduction

In the previous paper (Whitaker & Jeffery, 1970, subsequently referred to as WJ) the crystal structure determination of struvite is discussed. During the determination it was concluded that the ammonium ion was singly bonded to an oxygen atom and the ion then rotated about this bond as axis. This paper presents the evidence for this. The atomic designation is the same as in Whitaker & Jeffery (1970).

Experimental

The structure was solved and refined using anisotropic temperature factors until the residual remained sta-

* Now at The Department of Physics, Brunel University, London.