

5. Summary

In summary, the following appears to be experimentally well-established:

- The intensity of the *e* satellites in an An_{55} plagioclase owes its main contributions to atomic displacements and Ca/Na ordering (shown in T & F's paper).
- Displacements responsible for *e* satellites in an An_{55} plagioclase are preferentially oriented approximately parallel to the *b* axis (shown in § 3.1) and are larger than $\pm 0.25 \text{ \AA}$ (shown in § 4.1).
- To obtain the experimental value of the average intensity of *e* satellites, only a small portion of the atoms is required to have displacements as large as $\pm 0.3 \text{ \AA}$ (shown in § 4.3).

The following hypotheses appear to be plausible:

- Atoms displaced by $\pm 0.25 \text{ \AA}$ in the direction of the *b* axis and contributing strongly to *e* satellites are Na/Ca cations (discussed in § 4.2 and § 4.3).
- Na/Ca cations contribute strongly to *e* satellites but weakly to *f* satellites, which explains differences found in the intensity distribution of *e* and *f* satellites (discussed in § 4.4).

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Crystal Structure of Bis(cyclopentadienyl)beryllium at -120° *

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The crystal structure of bis(cyclopentadienyl)beryllium, $\text{Be}(\text{C}_5\text{H}_5)_2$ has been determined from X-ray diffraction photographs taken at -120°C . The crystals are monoclinic, space group $P2_1/n$, with cell dimensions $a = 5.95$ (3), $b = 7.51$ (2), $c = 8.94$ (3) \AA and $\beta = 92.8$ (5) $^\circ$. There are two molecules per unit cell. The final *R* value is 0.105. The two cyclopentadienyl rings are related by a centre to form a 'slip' sandwich. The normal distance between rings is 3.33 \AA . Two alternate positions are related by a centre for the disordered beryllium atoms. The Be is π -bonded to one of the rings with all Be–C distances equal to 1.94 (4) \AA . However, the Be appears to be σ -bonded to C(5') of the other ring, with a Be–C distance of 1.81 (5) \AA . This Be–C bond is normal to the plane of the ring. In the cyclopentadienyl rings, the carbon and hydrogen atoms are all coplanar, except H(5'). The observed H(5') positions suggest that the C(5')–H(5') bond forms an angle of about 30° with the plane, when C(5') is σ -bonded to Be. The calculated dipole moment, based on this structure, is in good agreement with the measured values.

Introduction

The compound bis(cyclopentadienyl)beryllium was first synthesized by Fischer & Hofmann (1959). It has been found to have a dipole moment of 2.46 D in benzene and 2.24 D in cyclohexane (Fischer & Schreiner, 1959). Careful electron diffraction studies of the gas phase of this compound (Almenningen, Bastiansen & Haaland, 1964; Haaland, 1968) showed that the molecule is of C_{5v} symmetry, with the rings

parallel and staggered. The Be atom occupies two alternative positions on the fivefold axis. However, since the structure in the solid state may not be the same as in the vapour state, and since it has been found that this compound has a very large temperature factor ($B \approx 18$) at room temperature (Wong, Chao, Chih & Lee, 1969), a low temperature X-ray diffraction study of this compound was undertaken.

Experimental

The compound was synthesized in this laboratory by the method of Fischer & Hofmann (1959). It is very sensitive to air and moisture. Single crystals were grown in thin-walled pyrex capillaries. Usually, they grow with the [111] direction parallel to the capillary axis, but sometimes with [100] or [001].

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The low-temperature setup was the boiling liquid-nitrogen type, described by Hirshfeld & Schmidt (1956). For data collection, the temperature at the sample was set at -120 (5) $^{\circ}\text{C}$. The equi-inclination,

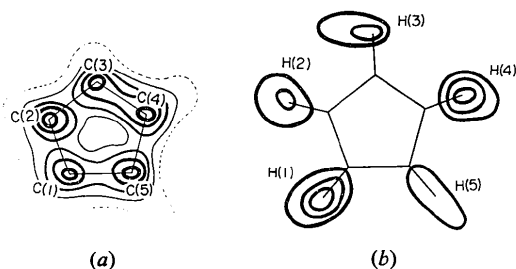


Fig. 1. Electron density map and difference map summed over the plane of the ring. (a) For carbon atoms, contours are at $1.5 \text{ e.}\text{\AA}^{-3}$. Dashed lines for zero contour. (b) For hydrogen atoms: first contour is at $0.3 \text{ e.}\text{\AA}^{-3}$, the next ones are at $0.15 \text{ e.}\text{\AA}^{-3}$. Negative contours are not shown.

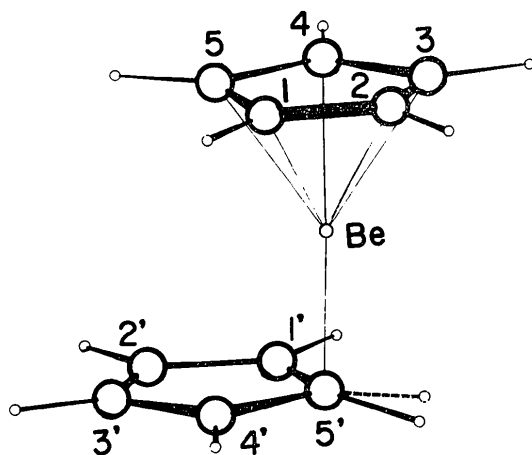


Fig. 2. The ordered molecular configuration of $\text{Be}(\text{C}_5\text{H}_5)_2$ at -120°C .

Table 1. The final parameters and their *e.s.d.*'s

The temperature factor is in the form of

$$T = \exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{31}lh).$$

The parameters have been multiplied by 10^4 , except those for hydrogen which have been multiplied by 10^3 . The temperature factors for hydrogen were fixed at $B=2.0$

C(1)	3971 (14)	6723 (12)	3272 (12)	223 (22)	129 (18)	85 (10)	183 (44)	95 (30)	-5 (48)
C(2)	5214 (14)	5677 (13)	2364 (10)	301 (27)	145 (20)	80 (11)	128 (49)	3 (37)	20 (48)
C(3)	7440 (14)	5584 (13)	3005 (11)	225 (24)	160 (21)	129 (14)	-62 (47)	88 (46)	-5 (41)
C(4)	7554 (13)	6521 (13)	4328 (12)	224 (24)	140 (20)	104 (13)	-113 (44)	68 (38)	-22 (39)
C(5)	5389 (15)	7260 (11)	4553 (11)	275 (23)	86 (17)	97 (14)	-56 (42)	96 (36)	-31 (38)
$\frac{1}{2}\text{Be}$	5319 (35)	4676 (24)	4363 (30)	260 (63)	51 (45)	100 (29)	-95 (88)	155 (84)	11 (89)
H(1)	228 (13)	686 (12)	292 (10)						
H(2)	467 (11)	500 (12)	136 (10)						
H(3)	870 (11)	495 (12)	243 (9)						
H(4)	882 (12)	661 (12)	495 (10)						
H(5)*	506 (14)	822 (12)	516 (11)						
$\frac{1}{2}\text{H}_a(5)^\dagger$	570	738	740						
$\frac{1}{2}\text{H}_b(5)^\dagger$	440	882	300						

* This is the least-squares result, which will make $\angle \text{H}(5)-\text{C}(5)-\text{CT} \sim 15^{\circ}$ (where CT is the centre of the ring) the average of our assumed values, 0° and 30° .

† Theoretical positions: $\text{H}_a(5)$ is on the plane of ring, whereas $\text{H}_b(5)$ will make $\angle \text{H}_b(5)-\text{C}(5)-\text{CT} \sim 30^{\circ}$.

multiple-film Weissenberg method, with Ni-filtered $\text{Cu } K\alpha$ radiation, was used for data collection. To minimize the exposure time, a Rigaku Denki rotating anode X-ray generator was used, reducing exposure time to one tenth of the normal time. Data collected were layers $0kl$, $h0l$, $hk0$, $hk1$, and $hk2$.* Intensities were estimated visually with a standard strip, prepared from the same crystal. Cell dimensions were determined by comparison with the powder pattern of gold ($a=4.0702 \text{ \AA}$), taken at room temperature and superposed on $0kl$ and $h0l$ Weissenberg photographs taken at -120°C . The cell dimensions are $a=5.95$ (3), $b=7.51$ (2), $c=8.94$ (3) \AA , and $\beta=92.8$ (5) $^{\circ}$. The number of molecules per unit cell was roughly estimated - by comparing the unit-cell volume with that of cyclopentadiene (Liebling & Marsh, 1965) - to be two. Altogether, 272 independent reflexions were recorded, of which 54 were too weak to be estimated. For each independent reflexion, the intensity was estimated at least twice, from different quadrants. After Lorentz & polarization corrections, the approximate parameters for the carbon and beryllium atoms, obtained from the preliminary report (Wong *et al.*, 1969), were refined by least-squares methods using isotropic temperature factors and a scale factor for each layer. The function minimized was $\sum \omega(F_o - F_c)^2$ and initially, unit weight was assigned to each reflexion. Two cycles of full-matrix least-squares calculations reduced R to 0.18 ($R = \sum |F_o - F_c| / \sum |F_o|$). The weight was then changed to F_o^2/F_c^2 for $F_o < F_c^0$ and F_c^0/F_o^2 for $F_o \geq F_c^0$, where $F_c^0 = 2.5$. This weight scheme was deduced from a plot of $|F_o|$'s vs. corresponding average deviations. Anisotropic temperature factors were introduced for C, while still using isotropic temperature factors for Be. Three cycles of least-squares refinement reduced R to 0.12. At this stage, all

* Crystals are sensitive to X-rays at low temperature and break up into several pieces after 4 to 5 hours of exposure. Also, due to the differences of thermal expansion coefficient, the crystals are easily loosened from the capillary walls on which they grow. Therefore, great pains have been taken in collecting these few layers of data.

five layers were placed on one scale and equivalent reflexions from different layers were averaged. A difference synthesis revealed the hydrogen atoms attached to atoms C(1), C(2), C(3) and C(4), with reasonable peak heights and positions. However, the hydrogen atom attached to C(5) appeared to be diffused (see Fig. 1). With the initial assumption that H(5) was in the plane of the ring, another three cycles of least-squares refinement were calculated, in which all the atoms, with anisotropic temperature factors for both carbon and beryllium and fixed isotropic temperature factors of $B=2.0$ for hydrogen, were included.

In the last cycle, the R value was 0.105, and the shifts were less than $\frac{1}{3}$ of their respective estimated standard deviations for the carbon atoms and less than $\frac{1}{2}$ their e.s.d. for the beryllium atoms. The shifts in most other temperature factors for C and Be, and in the positional parameters for H, were much less than the e.s.d., except in B_{22} of C(3) which is nearly equal to its e.s.d., and in the positional parameters of H(5), whose variations were always greater than their e.s.d. values. The resulting positions of H(5), although not very reliable, became such that C(H)–H(5) would form a 15° angle with the plane of the ring. A reasonable interpretation is that one half of H(5) lies in the plane of the ring and the remaining half is bent out about 30° away from the plane (Fig. 2). This would give an average value of 15° . Further refinement, with fixed values of $\frac{1}{2}H_a(5)$ and $\frac{1}{2}H_b(5)$ (see Table 1) included, gave no detectable improvement. The final parameters are listed in Table 1, and the observed and calculated structure factors in Table 2. Form factors used for Be^+ , C and H were taken from *International Tables for X-ray Crystallography* (1962). An electron density map and a difference map summed over the plane of the ring are shown in Fig. 1. In the final difference map, the maximum fluctuations were of the order of $0.3 \text{ e.}\text{\AA}^{-3}$.

Results and discussion

The crystal structure is disordered at -120°C . The ordered structure is shown in Fig. 2. It is reasonable to assume that the ring π -bonded to Be has equal C–C bond lengths of about 1.41 \AA corresponding to a 1.4 bond number, with all the hydrogen atoms in the plane of the ring, whereas the other ring has a regular cyclopentadiene structure (Liebling & Marsh, 1965) with C(5) σ -bonded to Be. The observed C–C bond lengths are in agreement with this assumption (Table 3). A possible explanation for the rather unusual configuration of the molecule is as follows. The normal interplanar distance for aromatic rings is about 3.4 \AA . If beryllium bis(cyclopentadienyl) has the usual sandwich structure, the interplanar distance will be approximately 3.2 \AA .[†] Apparently, the repulsion of the rings cannot be compensated for by the gain from the formation of a

Table 2. *Observed and calculated structure factors*

Values of $\frac{1}{2}H_a(5)$ and $\frac{1}{2}H_b(5)$ in Table 1 were used.

The five columns in each group represent $h, k, l, 2|F_o|$, and $2F_c$. Minus signs before $2|F_o|$ indicate unobserved reflexions which were given zero weight in the least-squares calculations.

0 0 2	61	-64	-1 2 2	59	-70	2 5 1	-10	4	1 1 1	29	26
0 0 4	79	85	-1 3 1	56	-53	2 5 2	12	-13	4 1 2	8	10
0 0 6	20	-22	-1 3 2	6	9	2 6 0	27	-25	4 2 2	27	28
0 0 8	50	-47	-1 4 1	30	32	2 6 1	-10	2	4 2 2	40	-28
0 0 10	19	-22	-1 4 2	143	122	2 6 2	30	-31	4 2 2	13	-42
0 1 1	125	127	-1 5 1	-1	-1	2 7 0	23	-23	4 3 0	9	-11
0 1 2	156	-180	-1 5 2	38	39	2 7 1	36	-35	4 3 1	-10	5
0 1 3	30	-29	-1 6 1	14	15	-3 0 1	116	111	4 3 2	27	-28
0 1 4	24	-23	1 0 1	222	226	-3 0 3	79	65	4 4 0	-10	5
0 1 5	24	23	1 0 3	55	55	-3 0 5	50	-55	4 4 1	52	-49
0 1 6	49	-53	1 0 5	73	76	-3 0 7	18	23	4 4 2	-9	8
0 1 7	26	-24	1 0 7	-9	4	-3 0 9	39	-50	4 5 0	9	15
0 1 8	22	-22	1 0 9	41	-50	-3 1 1	-8	14	4 5 2	-9	-9
0 1 9	29	-30	1 0 11	9	9	-3 1 3	31	32	4 6 0	21	-21
0 2 0	19	-17	1 1 0	142	152	-3 2 1	23	-25	4 6 2	19	18
0 2 1	168	-220	1 1 1	30	-34	-3 2 2	7	-1	-5 0 0	4	48
0 2 2	153	-145	1 1 2	-4	-10	-3 3 1	23	23	-5 0 3	18	12
0 2 3	27	19	1 2 0	97	96	-3 3 2	56	-58	-5 0 5	50	-55
0 2 4	30	31	1 2 1	-6	-3	-3 3 3	-10	-7	-5 0 7	21	-24
0 2 5	45	-44	1 2 2	2	9	-3 3 4	9	-5	-5 1 1	21	-24
0 2 6	26	-24	1 3 0	23	-21	-3 5 1	37	-44	-5 1 2	24	-24
0 2 7	21	-22	1 3 1	19	-15	-3 5 2	25	25	-5 1 3	11	-11
0 3 1	98	-96	1 3 2	18	18	-3 6 2	12	-13	-5 2 2	26	21
0 3 2	15	16	1 4 0	38	36	3 0 1	23	-25	-5 3 2	9	-6
0 3 3	25	23	1 4 1	43	43	3 0 3	42	45	-5 4 2	23	24
0 3 4	41	46	1 4 2	22	22	3 0 5	3	0	-5 5 2	15	15
0 3 5	-10	-15	1 5 0	32	28	3 0 7	18	-21	-5 6 2	15	17
0 3 6	-11	6	1 5 1	25	-24	3 0 9	9	9	-5 6 3	43	43
0 3 7	-11	13	1 5 2	22	24	3 1 0	53	5	-5 6 4	47	37
0 3 8	-11	14	1 6 0	-9	5	3 1 1	33	-36	-5 6 5	16	21
0 3 9	19	16	1 6 1	24	-24	3 1 3	60	-59	-5 6 7	14	10
0 4 0	-9	4	1 6 2	25	-24	3 2 0	66	-74	-5 7 0	10	-9
0 4 1	18	-17	1 7 0	31	-32	3 2 2	24	-24	-5 7 1	37	41
0 4 2	20	23	1 8 0	-8	3	3 2 2	20	15	-5 7 2	12	15
0 4 3	96	98	-2 0 2	49	46	3 3 0	18	20	-5 8 0	42	42
0 4 4	-10	-4	-2 0 4	20	-20	3 3 1	52	-53	-5 8 1	14	13
0 4 5	-11	9	-2 0 6	17	-15	3 3 2	21	16	-5 8 2	12	9
0 4 6	-11	2	-2 0 8	32	30	3 4 0	0	9	-5 9 0	27	29
0 4 7	39	40	-2 0 10	41	-40	3 4 1	38	36	-5 9 1	21	-20
0 5 1	40	39	-2 1 1	26	-27	3 4 2	2	9	-5 9 2	21	-20
0 5 2	21	23	-2 1 2	6	-14	3 5 0	13	3	-5 9 3	9	7
0 5 3	-11	-2	-2 1 3	34	35	-3 5 1	-10	3	-5 9 4	40	-40
0 5 4	-11	3	-2 2 2	45	-45	3 5 2	18	16	-5 9 5	17	18
0 5 5	-11	-4	-2 3 1	15	-15	3 6 0	9	9	-5 9 6	17	18
0 5 6	-11	12	-2 3 2	103	90	3 6 1	24	-25	-5 9 7	19	-15
0 5 7	-10	-5	-2 4 1	-9	-3	3 6 2	24	23	-6 0 0	17	-15
0 5 8	17	-17	-2 4 2	32	33	3 7 0	-8	-19	-6 0 1	8	6
0 5 9	19	-18	-2 5 1	40	39	3 7 1	17	-14	-6 0 2	25	-25
0 6 0	-11	7	-2 5 2	2	9	3 8 0	31	34	-6 0 3	30	-32
0 6 1	32	-31	2 0 0	30	34	-4 0 2	8	4	-6 1 2	11	22
0 6 2	12	15	2 0 2	19	-15	-4 0 4	17	-17	-6 2 1	9	14
0 6 3	16	17	2 0 4	83	90	-4 0 6	56	-58	-6 2 2	8	9
0 6 4	35	-36	2 0 6	18	-9	-4 0 8	33	-24	-6 3 1	12	20
0 7 2	-9	-11	2 0 8	23	20	-4 1 1	22	18	-6 3 2	27	30
0 8 0	20	-26	2 0 10	16	-12	-4 1 2	33	-37	-6 4 2	12	-12
0 8 1	-10	-5	2 1 0	28	-28	-4 2 1	33	-27	-6 5 2	16	-8
0 8 2	30	31	2 1 1	56	-58	-4 2 2	38	-45	6 0 0	27	-29
0 9 1	-7	0	2 1 2	47	48	-4 3 1	24	-18	6 0 2	16	17
0 9 2	-6	3	2 2 0	23	-24	-4 3 2	21	17	6 0 4	9	9
0 9 3	11	20	2 2 1	19	-16	-4 4 1	28	-28	6 1 0	22	24
-1 0 1	38	39	2 2 2	-6	-5	-4 4 2	9	-17	6 1 1	-9	2
-1 0 3	24	-18	2 3 0	-7	-6	-4 5 2	29	1	6 1 2	16	16
-1 0 5	19	-44	2 3 1	45	54	-4 6 2	30	33	6 2 1	25	19
-1 0 7	-9	-9	2 3 2	22	25	4 0 0	73	85	6 2 2	8	-3
-1 0 9	40	-11	2 4 0	53	54	4 0 2	-8	8	6 3 1	11	10
-1 1 1	149	-194	2 4 1	12	6	4 0 4	57	67	6 3 2	10	-10
-1 1 2	139	-133	2 4 2	68	69	4 0 6	24	-29	6 4 1	22	-17
-1 2 1	126	-162	2 5 0	47	37	4 1 0	15	14	6 4 2	16	11

Table 3. *Bond distances and bond angles*

C(1)–C(2)	1.37 (3) Å	C(5)–C(1)–C(2)	108 (5)°
C(2)–C(3)	1.42 (2)	C(1)–C(2)–C(3)	108 (5)
C(3)–C(4)	1.37 (3)	C(2)–C(3)–C(4)	109 (5)
C(4)–C(5)	1.43 (3)	C(3)–C(4)–C(5)	108 (5)
C(5)–C(1)	1.45 (3)	C(4)–C(5)–C(1)	106 (4)
Be—CT†	1.53 (5)	Be—C(5')—CT'	90 (5)
Be—C(1)	1.97 (4)	Be—CT—C(1)	90 (5)
Be—C(2)	1.94 (4)		
Be—C(3)	1.92 (5)		
Be—C(4)	1.92 (4)		
Be—C(5)	1.95 (3)		
Be—C(5')	1.81 (5)	Average of H–C–C angles is	125 (25)°.
Be—C(1')	2.38 (5)		
Be—C(4')	2.30 (5)		
C(1)–H(1)	1.05 (12)		
C(2)–H(2)	1.07 (15)		
C(3)–H(3)	1.04 (14)		
C(4)–H(4)	0.91 (12)		
C(5)–H(5)	0.94 (15)		

† Based on a ferrocene-like molecule with two pairs of electrons involved in π -bonding, giving a zero dipole moment.

† CT: centre of the ring.

regular sandwich structure. The observed interplanar distance of 3.33 Å and the 'slip' sandwich configuration is a compromise between the two opposing forces. Also, Be, with no *d* orbitals, is constrained to tetrahedral bonding and a cyclopentadienyl ring would occupy three orbitals of the metal atom, while the fourth orbital would have to form a σ -bond.

The best plane for the five carbon atoms is $0.2540X + 0.8214Y - 0.5107Z + 3.3015 = 0$ (referred to the coordinate system a^*, b, c). The deviations for C and H are: C(1) (0.01); C(2) (-0.01); C(3) (0.01); C(4) (0.00); C(5) (-0.01); H(1) (-0.01); H(2) (-0.09); H(3) (0.08); H(4) (0.00); and H(5) (0.26). At room temperature, Be moves freely between these two positions (Wong *et al.*, 1969), but at -120°C , it is frozen at one of the two.

The single-bond distance, Be-C, after correction for electronegativity difference, is 1.58 Å (Pauling, 1959; Schomaker & Stevenson, 1941). Thus, for the ring π -bonded to Be, each Be-C distance (average value, 1.94 Å) will have a bond number of 0.3. Therefore, there will be, in all, 1.5 pairs of electrons responsible for π -bonding. For the Be-C(5') σ -bond (1.81 Å), the bond number is 0.5. The partial ionic character of the Be-C bond is about 0.24 (Pauling, 1959). Based on this value, the charge distribution will be about +0.14 on the ring π -bonded to Be, +0.48 on Be, and -0.62 on the ring σ -bonded to Be.† The resulting dipole moment is 2.55D, in good agreement with the observed values

† This result is very similar to that which Professor Pauling has pointed out to Almenningen, Bastiansen & Haaland (1964).

of 2.46D in benzene and 2.24D in cyclohexane. The observed contacts between molecules are from 3.7 Å upwards for C to C, and 4.1 Å upwards for Be to C, showing that no intermolecular strain or association exists which might cause the difference between the electron diffraction model and the present one.

The molecular structure of this compound in the solid state is indeed different from its gas-state structure (C_{5v} symmetry) determined by electron diffraction (Almenningen, Bastiansen & Haaland, 1964; Haaland, 1968). The interatomic distances obtained from the solid-state model would not fit the radial distribution curves calculated from the electron diffraction patterns, beyond 3 Å.

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The Crystal Structure of Methyl Diammonium Phosphate Dihydrate, $(\text{NH}_4)_2\text{CH}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$

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$(\text{NH}_4)_2\text{CH}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ is orthorhombic, space group $P2_12_12_1$, with $a = 12.39$ (1), $b = 11.37$ (1), $c = 6.10$ (2) Å, and $Z = 4$. The structure was determined from Weissenberg film data, using Patterson and Fourier syntheses, and refined by the least-squares method with three-dimensional data (787 observed structure factors). The final *R* value, excluding the hydrogen atoms, is 0.090. A complex system of hydrogen bonds (twelve in the asymmetric unit) holds together the $\text{CH}_3\text{OPO}_3^-$ and NH_4^+ groups and the water molecules.

Introduction

During the course of studies on ammonium methyl-substituted phosphates (Gilli & Zani, 1972), crystals of methyl diammonium phosphate dihydrate, $(\text{NH}_4)_2\text{CH}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$ were prepared.

Literature on diammonium phosphate structures is scarce. Smith, Lehr & Brown (1957) published some crystallographic data of diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$, but not the complete structure, and Coates & Smith (1967) studied the dimorphism of the same compound. Recently, Khan, Straumanis &