

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  $\sigma$ -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  $-120^\circ\text{C}$ , 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  $\pi$ -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  $\pi$ -bonding. For the Be-C(5')  $\sigma$ -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  $\pi$ -bonded to Be, +0.48 on Be, and -0.62 on the ring  $\sigma$ -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  $\text{NH}_4^+$  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 &

Table 1. Observed and calculated structure factors

Unobserved structure factors are marked by an <. The zero weight *F*'s in the least-square refinement are indicated by an E.

H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>		
<E	0	0	2	87.4	176.8	1	1	4	17.5	14.4	2	1	3	26.4	25.8	3	1	4	22.0	19.9	4	1	7	11.8	13.6	
<E	0	0	6	64.1	67.7	1	1	5	6.8	5.2	2	1	4	5.7	5.5	3	1	5	26.2	23.9	4	2	0	10.8	11.1	
<E	0	0	6	2.1	1.8	1	1	6	7.4	7.4	2	1	5	10.8	11.1	3	1	6	10.9	11.1	4	2	1	31.5	30.7	
<E	0	0	1	40.1	55.0	1	1	7	1.5	2.6	2	1	6	6.0	5.9	3	1	7	17.9	14.0	4	2	2	18.8	15.9	
<E	0	0	1	2	6.0	6.1	1	2	0	51.5	91.5	2	1	7	8.4	7.4	3	2	0	17.1	14.8	4	2	3	23.7	24.5
<E	0	0	1	3	34.2	32.0	1	2	1	16.4	15.3	2	2	0	38.9	50.1	3	2	1	69.7	81.3	4	2	4	36.1	35.9
<E	0	0	1	4	30.1	29.3	1	2	2	25.0	25.3	2	2	1	26.7	29.4	3	2	2	6.1	4.6	4	2	5	17.7	17.9
<E	0	0	1	4	12.9	1.0	1	2	3	13.8	12.5	2	2	2	22.3	21.1	3	2	3	43.5	45.1	4	2	6	21.9	17.7
<E	0	0	1	5	16.2	16.6	1	2	4	25.6	24.1	2	2	3	12.8	12.7	3	2	4	14.5	13.5	4	2	7	11.5	7.3
<E	0	0	1	7	1.7	1.2	1	2	5	6.9	7.0	2	2	4	3.7	4.6	3	2	5	2.2	2.4	4	3	0	54.0	55.7
<E	0	0	2	22.2	20.4	<1	2	6	1.9	3.0	2	2	5	23.9	23.7	3	2	6	2.1	2.5	4	3	1	29.8	28.3	
<E	0	0	2	1	29.6	26.8	1	2	7	5.9	6.0	2	2	6	4.8	3.8	3	2	7	1.6	2.2	4	3	2	26.6	24.6
<E	0	0	2	6	8.2	7.7	1	3	0	16.7	17.6	2	2	7	15.6	14.1	3	3	0	31.1	28.2	4	3	3	28.7	27.5
<E	0	0	2	7	44.4	12.5	1	3	1	26.9	27.2	2	3	0	5.9	4.0	3	3	1	39.3	37.7	4	3	4	27.5	27.6
<E	0	0	2	7	37.5	43.2	1	3	2	15.9	15.4	2	3	1	27.4	23.3	3	3	2	23.5	22.4	4	3	5	20.4	20.8
<E	0	0	2	7	25.0	25.3	1	3	3	22.1	22.6	2	3	2	17.0	17.0	3	3	3	25.0	25.6	4	3	6	7.1	7.0
<E	0	0	2	7	12.9	8.9	1	3	4	33.1	30.9	2	3	3	5.5	4.2	3	3	4	24.9	23.4	4	3	7	11.1	10.8
<E	0	0	2	8	1.5	3.1	1	3	5	18.1	16.0	2	3	4	12.4	12.1	3	3	5	26.2	26.0	4	4	0	4.2	3.6
<E	0	0	2	8	6.4	6.1	1	3	6	12.3	12.0	2	3	5	9.5	9.6	3	3	6	11.3	12.2	4	4	1	7.4	5.0
<E	0	0	2	8	21.4	20.7	1	3	7	10.1	8.6	2	3	6	3.8	4.3	3	3	7	14.6	13.7	4	4	2	6.6	1.6
<E	0	0	2	8	33.4	35.4	1	4	0	27.5	29.1	2	3	7	4.4	4.7	3	4	0	37.0	33.5	4	4	3	9.6	9.2
<E	0	0	2	8	25.3	22.1	1	4	1	28.2	29.7	2	4	0	12.7	10.3	3	4	1	33.3	30.1	4	4	4	12.6	13.2
<E	0	0	2	8	2.1	.3	1	4	2	35.7	38.6	2	4	1	20.3	19.4	3	4	2	20.7	21.2	4	4	5	3.3	2.7
<E	0	0	2	8	13.3	13.6	1	4	3	19.6	20.5	2	4	2	1.5	2.8	3	4	2	36.6	35.8	4	4	6	5.9	3.7
<E	0	0	2	8	1.5	2.5	1	4	4	5.3	4.5	2	4	3	11.9	11.6	3	4	3	27.5	28.7	4	4	7	1.2	1.6
<E	0	0	2	8	76.9	127.6	1	4	5	19.8	18.9	2	4	4	18.0	17.6	3	4	5	28.4	28.6	4	4	8	12.9	11.4
<E	0	0	2	8	35.0	37.7	1	4	6	4.7	4.4	2	4	5	7.6	6.0	3	4	6	13.1	12.7	4	4	9	22.4	21.0
<E	0	0	2	8	58.2	68.4	1	4	7	11.1	10.1	2	4	6	6.7	6.9	3	4	7	14.9	14.9	4	4	10	1.8	1.4
<E	0	0	2	8	25.9	25.0	1	5	0	23.9	24.6	2	4	7	3.9	3.8	3	5	0	48.5	48.0	4	4	11	10.4	11.4
<E	0	0	2	8	37.1	39.7	1	5	1	11.2	9.9	2	5	0	12.1	11.2	3	5	1	35.6	32.6	4	4	12	6.0	5.4
<E	0	0	2	8	29.5	27.9	1	5	2	20.2	20.7	2	5	1	31.5	32.0	3	5	2	22.8	21.9	4	4	13	18.5	19.6
<E	0	0	2	8	5.9	4.0	1	5	3	13.8	13.7	2	5	2	18.1	18.3	3	5	3	27.1	27.1	4	4	14	3.6	3.4
<E	0	0	2	8	14.8	13.5	1	5	4	4.7	3.4	2	5	3	17.8	18.6	3	5	4	22.4	24.5	4	4	15	7.2	8.2
<E	0	0	2	8	34.7	33.7	<1	5	5	2.0	2.3	2	5	4	25.0	26.4	3	5	5	7.8	9.3	4	4	16	3.9	5.5
<E	0	0	2	8	38.8	37.3	1	5	6	5.1	5.4	2	5	5	16.9	18.8	3	5	6	6.0	6.9	4	4	17	14.4	12.5
<E	0	0	2	8	14.9	11.9	1	5	7	4.3	2.8	2	5	6	13.0	12.8	3	5	7	7.1	7.0	4	4	18	8.1	8.4
<E	0	0	2	8	48.4	50.3	1	6	0	31.1	32.0	2	5	7	8.2	8.1	3	6	0	24.8	22.5	4	4	19	20.0	20.1
<E	0	0	2	8	2.2	1.8	1	6	1	31.1	32.1	2	6	0	11.6	12.8	3	6	1	43.9	39.5	4	4	20	15.5	16.0
<E	0	0	2	8	22.4	22.8	1	6	2	17.1	16.9	2	6	1	9.2	6.5	3	6	2	20.8	19.5	4	4	21	9.7	11.2
<E	0	0	2	8	5.6	5.3	1	6	3	18.2	18.7	2	6	2	6.7	4.3	3	6	3	21.9	21.8	4	4	22	5.4	5.4
<E	0	0	2	8	4.6	5	1	6	4	10.0	10.7	2	6	3	7.3	7.5	3	6	4	20.9	22.1	4	4	23	55.9	59.5
<E	0	0	2	8	10.0	9.3	1	6	5	17.6	18.3	2	6	4	9.4	11.0	3	6	5	10.0	10.1	4	4	24	33.7	33.1
<E	0	0	2	8	14.7	14.5	1	6	6	5.7	6.0	2	6	5	10.5	10.7	3	6	6	5.2	5.9	4	4	25	33.3	35.1
<E	0	0	2	8	14.6	13.4	1	6	7	6.9	7.2	2	6	6	1.7	2.1	3	6	7	1.9	1.6	4	4	26	15.2	16.5
<E	0	0	2	8	10.4	8.2	1	7	0	4.3	3.3	2	6	7	10.6	9.7	3	6	8	15.2	13.1	4	4	27	19.7	22.4
<E	0	0	2	8	18.9	18.9	1	7	1	20.6	22.4	2	7	0	12.6	10.9	3	6	9	11.1	9.7	4	4	28	20.7	1.0
<E	0	0	2	8	1.8	1.0	1	7	2	10.2	10.6	2	7	1	9.6	10.8	3	6	10	11.1	11.3	4	4	29	2.6	2.4
<E	0	0	2	8	13.0	13.3	1	7	3	10.5	10.6	2	7	2	3.2	3.2	3	6	11	11.4	11.0	4	4	30	9.3	7.5
<E	0	0	2	8	30.3	27.4	1	7	4	22.5	23.7	2	7	3	3.4	4.2	3	6	12	17.6	16.5	4	4	31	23.9	21.3
<E	0	0	2	8	5.7	7.2	1	7	5	13.1	13.2	2	7	4	6.4	7.7	3	6	13	10.2	9.0	4	4	32	5.4	5.4
<E	0	0	2	8	19.8	20.0	1	7	6	15.6	15.1	2	7	5	9.6	9.6	3	6	14	33.3	31.1	4	4	33	11.5	10.8
<E	0	0	2	8	9.3	10.2	1	8	0	12.2	8.6	2	7	6	5.9	5.3	3	6	15	28.9	29.4	4	4	34	7.0	6.8
<E	0	0	2	8	2.1	.8	1	8	1	5.7	5.1	2	8	0	22.4	23.3	3	6	16	16.3	16.2	4	4	35	1.8	2.0
<E	0	0	2	8	1.6	3.2	1	8	2	6.3	7.4	2	8	1	24.8	23.8	3	6	17	21.0	22.5	4	4	36	3.6	3.7
<E	0	0	2	8	24.1	23.8	1	8	3	11.1	10.6	2	8	2	17.1	18.0	3	6	18	9.9	11.8	4	4	37	9.9	7.4
<E	0	0	2	8	20.7	17.9	<1	8	4	2.0	2.8	2	8	3	10.9	12.5	3	6	19	11.7	9.0	4	4	38	7.4	7.1
<E	0	0	2	8	17.7	17.9	1	8	5	11.7	11.4	2	8	4	7.7	7.8	3	6	20	11.2	10.6	4	4	39	5.3	6.2
<E	0	0	2	8	12.7	13.6	1	8	6	6.7	5.3	2	8	5	6.6	8.1	3	6	21	37.9	32.4	4	4	40	7.3	6.4
<E	0	0	2	8	2.1	1.9	1	9	0	8.3	8.9	2	8	6	1.3	1.8	3	6	22	31.3	28.2	4	4	41	2.6	2.6
<E	0	0	2	8	19.3	21.4	1	9	1	12.7	13.1	2	9	0	7.7	7.0	3	6	23	21.9	22.2	4	4	42	12.9	10.8
<E	0	0	2	8	6.8	5.9	1	9	2	10.2	10.5	2	9	1	9.6	10.0	3	6	24	18.1	18.7	4	4	43	15.7	16.4
<E	0	0	2	8	9.6	7																				

Table 1 (cont.)

H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	
5	5	0	16.5	15.8	7	2	3	20.2	23.6	9	2	1	31.4	32.2	11	4	1	6.2	6.6	<14	1	3	4.5	3.4	
5	5	1	14.8	13.4	7	3	0	7.7	6.0	9	2	2	15.2	14.3	11	4	2	11.7	11.5	<14	2	0	1.8	6.9	
5	5	2	1.9	2.3	7	3	1	14.8	15.2	9	2	3	18.8	19.6	11	4	3	5.7	6.0	<14	2	1	4.9	4.1	
5	5	3	10.9	12.8	7	3	2	4.6	5.2	9	3	0	11.3	10.7	11	5	0	11.2	10.6	<14	2	2	6.7	4.9	
5	5	6	0	11.9	11.1	7	3	3	9.8	10.7	9	3	1	28.3	26.9	<11	5	1	2.1	3.8	<14	2	3	10.6	8.7
5	5	6	1	23.9	23.9	<7	4	0	1.8	.6	9	3	2	10.8	11.1	<11	5	2	2.0	3.6	<14	3	0	10.5	9.4
5	5	6	2	8.9	7.5	<7	4	1	13.7	13.4	9	3	3	20.6	21.9	<11	5	3	6.9	7.3	<14	3	1	5.0	3.9
5	5	6	3	16.1	17.5	7	4	2	20.7	22.2	9	4	0	10.0	7.1	11	6	0	14.1	11.3	<14	3	2	7.9	6.0
5	5	7	0	7.0	5.1	7	4	3	13.8	13.5	9	4	1	13.6	12.1	11	6	1	7.4	7.8	<14	3	3	6.8	5.1
5	5	7	1	6.4	6.3	7	5	0	30.9	31.2	9	4	2	5.5	6.4	11	6	2	8.1	6.8	<14	4	0	1.7	.5
5	5	7	2	12.9	13.3	7	5	1	16.7	16.7	9	4	3	12.6	12.4	11	6	3	6.8	6.6	<14	4	1	9.1	6.4
5	5	7	3	5.3	6.0	7	5	2	16.9	16.9	<9	5	0	2.2	1.7	<11	7	0	1.9	2.0	<14	4	2	1.4	1.3
5	5	8	0	2.1	.4	7	5	3	12.7	14.1	<9	5	1	10.9	9.8	11	7	1	5.8	6.3	<14	5	0	4.1	2.3
5	5	8	1	22.9	23.6	<7	6	0	2.0	2.8	<9	5	2	2.2	.9	11	7	2	6.5	6.0	<14	5	1	5.1	5.6
5	5	8	2	2.2	2.4	<7	6	1	26.2	25.2	<9	5	3	8.9	10.0	<11	7	3	4.7	4.5	<14	6	0	6.5	5.0
5	5	8	3	16.4	16.9	7	6	2	9.6	11.0	9	6	0	22.2	21.9	<11	8	0	1.7	1.2	<14	6	1	4.0	3.2
5	5	9	0	31.0	29.1	7	6	3	13.1	14.6	9	6	1	24.6	22.3	<11	8	1	1.5	1.8	<15	0	1	1.7	.7
5	5	9	1	11.2	11.0	7	7	0	18.0	6.8	9	6	2	16.7	17.7	<11	8	2	6.8	5.4	<15	0	2	4.7	3.8
5	5	9	2	17.6	18.0	7	7	1	9.5	10.5	9	7	0	6.0	6.2	<11	9	0	1.5	2.3	<15	1	0	7.3	6.4
5	5	9	3	10.5	11.4	7	7	2	21.5	22.3	9	7	1	9.8	9.7	11	9	1	8.6	7.2	<15	1	1	7.5	6.8
5	5	10	0	5.3	3.0	7	7	3	5.1	4.9	9	7	2	9.2	7.8	11	9	2	4.3	3.4	<15	2	0	1.1	1.1
5	5	10	1	17.6	18.1	7	8	0	11.3	9.8	9	7	3	11.2	11.2	<11	10	0	1.1	.4	<15	2	1	7.2	7.2
5	5	10	2	2.1	2.8	7	8	1	21.1	19.2	9	7	4	15.0	10.2	<11	10	1	3.9	2.9	<15	2	2	.8	1.4
5	5	10	3	10.0	12.2	7	8	2	5.9	5.2	9	8	0	13.3	9.1	<12	0	0	34.0	34.3	<15	2	3	1.0	.1
5	5	11	0	2.0	3.2	7	8	3	13.1	14.2	<9	8	1	2.0	1.1	<12	0	1	2.0	1.1	<15	3	0	6.1	5.6
5	5	11	1	2.0	4.3	7	9	0	29.0	26.5	<9	8	2	2.0	1.1	<12	0	2	19.8	20.1	<15	3	1	6.1	5.6
5	5	11	2	9.7	9.7	7	9	1	10.7	11.0	<9	9	0	3.0	2.0	<12	0	3	1.7	1.8	<15	3	2	.7	1.7
5	5	11	3	7.7	6.6	7	9	2	17.0	17.3	<9	9	1	12.8	12.7	<12	1	0	7.5	7.6	<15	4	0	.9	1.5
5	5	12	0	1.8	1.8	7	9	3	7.2	6.8	<9	9	2	1.8	3.1	<12	1	1	9.8	9.9	<15	4	1	5.8	5.1
5	5	12	1	1.8	1.7	7	10	0	6.1	5.6	<9	9	3	8.8	7.3	<12	1	2	1.9	3.5					
5	5	12	2	4.5	4.8	7	10	1	8.4	7.0	<9	9	4	1.8	3.9	<12	1	3	6.2	6.9					
5	5	12	3	3.6	2.7	7	10	2	4.6	4.8	<9	10	0	7.4	6.2	<12	2	0	8.9	7.6					
5	5	13	0	14.9	11.9	7	10	3	4.2	4.3	9	10	1	5.1	6.6	<12	2	1	6.4	6.4					
5	5	13	1	6.6	4.4	<7	11	0	1.8	1.2	9	10	2	6.6	6.9	<12	2	2	1.9	3.5					
5	5	13	2	12.8	12.1	<7	11	1	5.3	4.8	9	10	3	8.9	8.0	<12	2	3	1.2	1.4					
5	6	0	0	18.8	16.6	<7	11	2	1.5	3.9	9	11	0	10.4	9.2	<12	3	0	5.7	5.3					
5	6	0	1	10.4	9.8	<7	11	3	12.5	10.8	9	11	1	10.4	9.2	<12	3	1	9.7	8.6					
5	6	0	2	1.7	2.8	7	12	0	8.1	7.0	9	11	2	10.3	9.8	<12	3	2	6.9	7.8					
5	6	0	3	10.7	11.8	7	12	1	12.5	9.3	<9	12	0	.9	6.4	<12	3	3	7.4	8.3					
5	6	1	0	47.0	45.0	7	12	2	7.9	7.1	10	0	0	54.9	57.4	<12	3	4	19.7	18.6					
5	6	1	1	15.3	13.1	<7	13	0	.9	5.8	10	0	1	16.1	16.8	<12	4	0	8.6	8.2					
5	6	1	2	21.7	20.3	8	0	0	19.7	21.5	10	0	2	29.8	32.5	<12	4	1	12.6	12.7					
5	6	1	3	4.2	3.1	8	0	1	29.1	28.4	<10	0	3	1.9	4.3	<12	4	2	4.8	5.3					
5	6	2	0	7.5	4.6	<8	0	2	2.0	2.1	10	1	0	17.5	15.8	<12	5	0	2.0	2.0					
5	6	2	1	41.2	37.8	8	0	3	15.5	15.6	10	1	1	21.1	19.8	<12	5	1	7.5	7.9					
5	6	2	2	32.7	33.3	8	1	0	8.2	7.1	10	1	2	13.8	13.7	<12	5	2	9.6	10.0					
5	6	2	3	17.1	18.3	8	1	1	17.0	16.1	10	2	0	8.3	7.8	<12	5	3	3.4	3.6					
5	6	3	0	64.3	65.9	<8	1	2	2.0	3.4	10	2	1	12.5	12.8	<12	6	0	10.0	7.9					
5	6	3	1	14.8	15.0	<8	1	3	15.5	16.9	10	2	2	2.0	1.9	<12	6	1	4.2	4.4					
5	6	3	2	29.4	30.9	8	2	0	8.5	8.7	<10	2	3	5.2	6.4	<12	6	2	4.9	4.3					
5	6	3	3	22.0	23.6	8	2	1	15.8	15.8	<10	2	4	2.0	2.3	<12	6	3	6.6	7.4					
5	6	3	4	9.1	7.0	8	2	2	2.1	2.8	<10	3	0	14.0	12.4	<12	7	0	1.6	1.6					
5	6	4	0	5.6	6.4	8	2	3	9.2	10.8	10	3	1	6.6	5.6	<12	7	1	13.2	10.1					
5	6	4	1	1.9	2.5	8	3	0	14.9	14.1	10	3	2	10.5	12.2	<12	7	2	7.9	7.9					
5	6	4	2	13.6	14.4	8	3	1	7.4	8.1	10	3	3	30.5	30.5	<12	7	3	14.9	13.7					
5	6	4	3	10.1	9.2	8	3	2	5.4	6.4	10	4	0	14.3	13.3	<12	8	0	9.6	8.5					
5	6	5	0	19.2	19.9	8	3	3	12.1	12.1	10	4	1	17.6	19.2	<12	8	1	10.6	10.8					
5	6	5	1	10.0	10.8	8	4	0	7.3	8.0	10	4	2	9.4	9.7	<12	8	2	1.1	1.8					
5	6	5	2	15.5	15.9	8	4	1	6.2	7.4	10	4	3	11.4	9.2	<12	9	0	4.0	3.7					
5	6	6	0	2.0	1.7	8	4	2	5.5	6.6	10	5	0	13.9	14.2	<12	9	1	6.2	5.3					
5	6	6	1	27.0	23.8	8	4	3	6.8	7.2	10	5	1	15.3	14.0	<13	0	1	1.5	.7					
5	6	6	2	14.3	13.7	8	5	0	15.8	11.4	10	5	2	12.7	14.0	<13	0	2	9.3	9.2					
5	6	6	3	19.1	22.2	8	5	1	18.4	16.9	10	5	3	7.5	5.8	<13	0	3	7.8	7.8					
5	6	7	0	62.4	60.7	8	5	2	9.4	9.0	10	6	0	6.5	4.3	<13	1	0	14.6	16.3					
5	6	7	1	10.0	9.2	8	5	3	12.4	13.0	<10	6	1	1.9	2.7	<13	1	1	6.2	6.5					
5	6	7	2	36.1	38.5	8	6	0	6.6	7.0	<10	6	2	6.7	6.9	<13	1	2	9.4	9.9					
5	6	7	3	5.0	5.6	8	6	1	17.8	17.2	<10	7	0	1.9	1.0	<13	1	3	11.4	10.8					
5	6	8	0	5.3	5.0	8																			

### Experimental

Colourless elongated crystals were grown from a solution in ethanol at 95%. Details of synthesis and chemical analysis can be found in the paper of Gilli & Zani (1972).

X-ray data were taken using two crystals with transverse dimensions less than 0.2 mm around the major axis of the crystal  $c$ , and around  $a$ .

Weissenberg photographs showed the space group extinctions  $h=2n+1$  for  $h00$ ,  $k=2n+1$  for  $0k0$  and  $l=2n+1$  for  $00l$ ; the space group is therefore  $P2_12_12_1$ .

The unit-cell constants, obtained from rotation and zero-layer Weissenberg photographs, are:

$$a=12.39 (1), b=11.37 (1), c=6.10 (2) \text{ \AA}, \\ Z=4, V=859.3 \text{ \AA}^3.$$

The calculated density ( $1.41 \text{ g.cm}^{-3}$ ) may be compared with  $1.47 \text{ g.cm}^{-3}$ , measured by flotation.

Cu  $K\alpha$  intensity data, with  $\sin \theta \leq 0.98$  were measured from multi-film Weissenberg photographs; 787 independent values were used in the structure determination. Lorentz and polarization, and Phillips (1954) corrections were applied on the observed intensities.

### Determination and refinement of crystal structure

The phosphorus atom was located from a sharpened three-dimensional Patterson synthesis ( $R=0.42$ ). The sharpened coefficients were obtained by dividing each  $F^2$  by  $\sum n_j f_j^2$ .

The remainder of the non-hydrogen atoms were located by means of three-dimensional electron density syntheses. A structure factor calculation based on approximate atom coordinates, excepting those of the water of crystallization and all hydrogen atoms, gave  $R=0.35$ . The atomic scattering factors were calculated according to Vand, Eiland & Pepinsky (1957), using the values suggested by Moore (1963) for the constants  $A_j, B_j, C_j, a_j, b_j$ .

A full-matrix least-squares refinement was carried out with a program prepared by Immirzi (1967). The weighting scheme suggested by Cruickshank (1965) was used, with  $A=25.0, B=1.0, C=0.016$ .

The 143 non-observed structure factors with  $\sin \theta \leq 0.98$  were given a value equal to one half of the observable limit, and a weight constant of 0.05.

Four isotropic least-square cycles lowered  $R$  to 0.185 and, at this stage, a Fourier synthesis allowed the two water molecules of crystallization to be located. Four subsequent isotropic cycles reduced  $R$  to 0.122.

The introduction of anisotropic thermal factors did not significantly lower the reliability index ( $R=0.106$ ) and the elimination of three low-angle reflexions probably suffering from secondary extinction effects, gave rise to a final  $R$  of 0.090 (0.097 with non-observed factors). An attempt was made to reveal the hydrogen atom positions from a difference map, but this was unsuccessful.

Table 1 lists observed and calculated structure factors. Final atomic parameters with their standard deviations are given in Table 2 and the anisotropic thermal parameters are presented in Table 3.

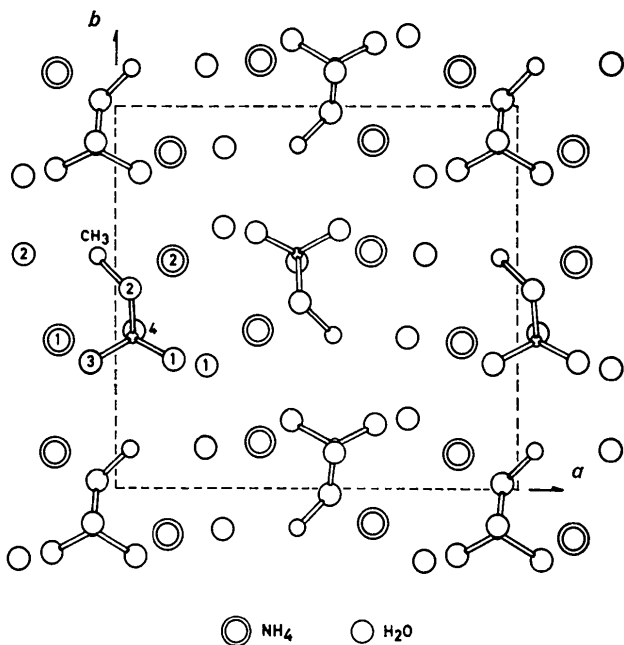


Fig. 1. A general projection along  $c$  of the  $(\text{NH}_4)_2\text{CH}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$  structure. The atoms are labelled as in Table 2.

Table 2. Fractional atomic parameters and their standard deviations

	$x/a$	$y/b$	$z/c$
P	0.0451 (2)	0.3885 (2)	0.4578 (3)
O(1)	0.1441 (5)	0.3345 (5)	0.5572 (12)
O(2)	0.0389 (5)	0.5144 (5)	0.5729 (13)
O(3)	-0.0606 (5)	0.3269 (5)	0.5150 (12)
O(4)	0.0533 (5)	0.4099 (6)	0.2165 (10)
C	-0.0392 (9)	0.6038 (7)	0.5045 (25)
N(1)	-0.1319 (6)	0.3809 (7)	0.9555 (13)
N(2)	0.1437 (7)	0.5971 (6)	0.9664 (14)
O(w1)	0.2282 (6)	0.3161 (6)	0.9785 (12)
O(w2)	0.2245 (6)	0.1070 (6)	0.5342 (17)

### Discussion of the structure

Fig. 1 shows a projection along the  $c$  axis of the whole content of the orthorhombic unit cell.

#### The $\text{CH}_3\text{OPO}_3^{2-}$ group

The bond distances and angles of the  $\text{CH}_3\text{OPO}_3^{2-}$  group are listed with their standard deviations in Table 4.

In the phosphate tetrahedron there are three short P-O bonds with an average value of  $1.507 \text{ \AA}$ . The longest one is the P-O(2) bond, where O(2) is the oxygen

Table 3. Anisotropic thermal parameters  $B_{1j}$  and their standard deviationsTemperature factor =  $\exp [-\frac{1}{4}(B_{11}a^*2h^2 + B_{22}b^*2k^2 + B_{33}c^*2l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$ 

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	1.85 (6)	1.45 (6)	0.80 (7)	-0.04 (5)	-0.08 (8)	0.04 (6)
O(1)	2.54 (21)	2.50 (22)	2.63 (28)	0.94 (20)	-1.02 (28)	0.45 (25)
O(2)	3.21 (25)	1.63 (19)	3.25 (32)	0.33 (19)	-0.45 (33)	-0.70 (22)
O(3)	2.84 (21)	1.81 (18)	2.64 (26)	-0.61 (18)	-0.46 (28)	0.65 (22)
O(4)	2.44 (23)	3.42 (25)	1.07 (21)	0.18 (21)	-0.41 (26)	-0.28 (21)
C	4.50 (47)	1.57 (29)	5.73 (63)	0.95 (30)	-0.95 (64)	-0.03 (42)
N(1)	3.22 (29)	2.67 (27)	1.83 (31)	0.47 (25)	-0.42 (36)	-0.52 (30)
N(2)	3.99 (32)	2.09 (26)	2.04 (32)	-0.80 (25)	-0.41 (38)	-0.04 (27)
O(w1)	3.73 (27)	2.92 (25)	2.56 (27)	0.66 (24)	0.66 (34)	-0.05 (29)
O(w2)	4.15 (30)	2.10 (24)	6.26 (49)	-0.25 (22)	1.09 (42)	0.19 (35)

Table 4. Bond lengths and angles with their standard deviations

P-O(1)	1.500 (7) Å	O(1)-P-O(2)	103.2 (3)
P-O(2)	1.597 (6)	O(1)-P-O(3)	114.0 (4)
P-O(3)	1.525 (7)	O(1)-P-O(4)	114.2 (3)
P-O(4)	1.495 (6)	O(2)-P-O(3)	105.7 (3)
		O(2)-P-O(4)	106.9 (2)
O(2)-C	1.464 (12)	O(3)-P-O(4)	111.0 (3)
		P-O(2)-C	121.9 (6)

bonded to the methyl group. The average value for all the P-O bonds is 1.529 Å.

The O-P-O angles can be divided into two classes with a value larger or smaller ( $\sim 105^\circ$ ) than  $109.5^\circ$ . In accordance with the close-packing principle, the longest P-O(2) bond is involved in all the smaller O-P-O angles.

A comparison of the values of bond lengths and valence angles in the phosphate groups has been made recently by Karle & Britts (1966) for organic phosphates, by Sundaralingam & Putkey (1970) for mono-anionic monophosphates, and by Baur & Khan (1970). The longest bond P-O(2) = 1.597 Å is in good agreement with the P-OR values found by Sundaralingam & Putkey (1970), and with the P-O(*l*) values (*l* = longer) found by Baur & Khan (1970). The average value of the other P-O bonds lies within the limits cited by the above mentioned authors, if the values of P-OH lengths are excluded.

The bond lengths obtained by us are very similar to those obtained by Trueblood, Horn & Luzzati (1961) for calcium thymidylate, with schematic formula  $R-CH_2OPO_3^{2-}Ca^{+2}$ . The values obtained by these authors are 1.587 Å for P-OR and 1.474, 1.486, and 1.514 Å for the other P-O bonds.

The values of the O-P-O angles are in good agreement with the references cited by Baur & Khan (1970).

The lengths of PO-C bonds found in various organic phosphates and listed by Sundaralingam & Putkey (1970), have values from 1.429 Å to 1.475 Å. The length of the PO-C bond in our crystal is 1.464 Å. The same value was found by Carlisle & Cook (1969) in thiamine pyrophosphate. The angle P-O-C of  $121.9^\circ$  agrees with the values already cited.

As expected, the CH<sub>3</sub> group is staggered with respect to the oxygen atoms of the PO<sub>4</sub> group.

#### Hydrogen bonding

In Table 5 are listed the N-O and O-O distances shorter than 3.3 Å. There are twelve contacts with values lying between 2.78 and 2.90 Å, with standard deviations of about 0.011 Å.

Table 5. Interatomic distances less than 3.3 Å

N(2)-O(1)	2.796 Å
N(2)-O(2)	2.886
N(2)-O(3)	2.810
N(2)-O(4)	2.850
N(1)-O(3)	2.893
N(1)-O(4)	2.812
N(1)-O(w1)	2.860
N(1)-O(w2)	2.818
O(w1)-O(1)	2.779
O(w1)-O(4)	2.817
O(w2)-O(1)	2.773
O(w2)-O(3)	2.781

Each of the oxygen atoms of the phosphate group, which are not bonded to a carbon atom, is at the centre of a distorted tetrahedron, the vertices of which are the phosphorus and three nitrogen or oxygen atoms belonging to NH<sub>4</sub><sup>+</sup> or H<sub>2</sub>O respectively. The O(2), linked with the methyl group, has only one hydrogen contact with an ammonium ion as the donor.

The ammonium ions can also be considered to be at the centre of distorted tetrahedra. One of these, N(1), is bonded to two molecules of water and two oxygen atoms of two different phosphate groups; the other, N(2), is in contact with four oxygen atoms belonging to four different PO<sub>4</sub> groups.

Each water molecule is involved in three hydrogen bonds. Both O(w1) and O(w2) are bonded to two oxygen atoms of the phosphate groups and one ammonium ion.

A three-dimensional view of the structure is shown in Fig. 2, where arrows indicate the hydrogen bonds. It is possible to see that N(1), N(2) and O(w1) are hydrogen bonded with two equivalent phosphate groups.

As in other organic phosphates (Sundaralingam & Putkey, 1970), hydrophobic channels, where methyl groups are present, run in the [001] direction.

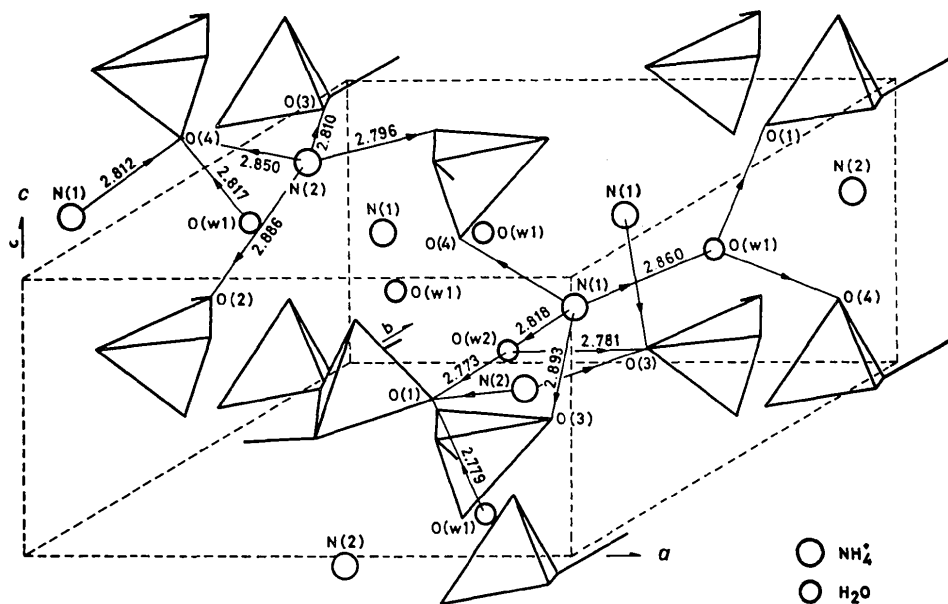


Fig. 2. A general three-dimensional view of the  $(\text{NH}_4)_2\text{CH}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$  structure. Tetrahedra represent the  $\text{PO}_4$  groups with P at the centre; circles represent the N and O atoms belonging to  $\text{NH}_4^+$  ions or  $\text{H}_2\text{O}$  molecules. Arrows indicate the hydrogen bonds.

Table 6. Values of the angles of the coordination polyhedra around  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$

Angle		
N(1)	O(3)—N(1)—O(4)	107.5°
	O(3)—N(1)—O(w1)	96.6
	O(3)—N(1)—O(w2)	109.5
	O(4)—N(1)—O(w1)	120.3
	O(4)—N(1)—O(w2)	100.2
N(2)	O(w1)—N(1)—O(w2)	117.4
	O(1)—N(2)—O(2)	132.4
	O(1)—N(2)—O(3)	94.5
	O(1)—N(2)—O(4)	118.0
	O(2)—N(2)—O(3)	99.9
O(w1)	O(2)—N(2)—O(4)	91.3
	O(3)—N(2)—O(4)	121.8
	O(1)—O(w1)—O(4)	99.2
	O(1)—O(w1)—N(1)	118.2
	N(1)—O(w1)—O(4)	133.6
O(w2)	O(1)—O(w2)—O(3)	95.4
	O(1)—O(w2)—N(1)	134.5
	N(1)—O(w2)—O(3)	129.4

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