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The Crystal Structure of Ammoniumtetrametaphosphate, $(NH_4)_4P_4O_{12}$

By C. Romers

Polytechnic Institute, University of Indonesia, Bandung, Java,

and J. A. A. Ketelaar and C. H. MacGillavry

Laboratory for General and Inorganic Chemistry, University of Amsterdam, Holland

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The crystal of ammoniumtetrametaphosphate is shown by X-ray analysis to be built from tetramer anions P_4O_{12}, and from NH_4 ions. Anions and cations form alternating layers parallel to (010). The ammonium ions form hydrogen bonds with oxygen atoms in roughly tetrahedral directions. P–O distances show the same general features as in phosphorus pentoxide and related compounds.

1. Introduction

The investigation of the crystal structure of ammoniumtetrametaphosphate (ATMP) was started several years ago by one of us (Ketelaar, with Dijkhoff, van Santen, 't Hart & Wijmenga, 1937). Although cell constants, space group and general features of the structure were determined at that time, no satisfactory agreement between calculated and observed structure factors was obtained. We therefore decided a few years ago to resume the investigation.

ATMP crystals were made following Warschauer (1903). Optical investigation had already shown that the crystals are biaxial, negatively birefringent, so that the symmetry cannot be tetragonal as stated by Warschauer. Goniometric measurements show indeed that the crystal class is $2/m\,2/m\,2/m$. Holohedry was confirmed by the complete lack of piezo-electricity. (We are indebted to Dr W. G. Perdok (Groningen) for a thorough check on this point.)

2. Unit cell and space group

Rotation photographs about [100], [010] and [001] were made, also Weissenberg diagrams of the reciprocal planes $0kl$, $1kl$, $h0l$, $h1l$, $hk0$ and hhl, all with Cu K radiation. Since the diagrams showed strong spots up to θ near 90°, Weissenberg diagrams $0kl$, $h0l$ and hhl were also made with Mo K radiation in order to avoid termination-of-series effects in Patterson and Fourier syntheses.

The following systematic absences were observed: hkl with $h+k$ odd, $hk0$ with h odd and k odd, $h0l$ with h odd and l odd. Thus the space group is *Cmca*. The cell constants are

$$a = 10{\cdot}4_2,\quad b = 10{\cdot}8_2,\quad c = 12{\cdot}7_8\text{ A.}$$

From the density of $1{\cdot}811$ g.cm.$^{-3}$ one finds that the unit cell contains 16 molecules NH_4PO_3.

3. Trial analysis

Pauling & Sherman (1937) showed that, in the structure of aluminium metaphosphate, anions P_4O_{12} are present in which four PO_4 tetrahedra are linked by two corners each to form a ring. Also, Warschauer's conductivity measurements on ATMP led him to assume a tetramer formula for the metaphosphate ion in this compound. Indeed, the presence of such an anion is more or less suggested by the space group *Cmca*: in the two sets of fourfold position $4a$ and $4b$ the point symmetry is $2/m$, so it is plausible that the 16 P atoms are clustered around either $4a$ or $4b$ in groups of four. There are several ways in which the group P_4O_{12} can be located so as to comply with the point-group symmetry $2/m$, but only in one case could a rough agreement for the intensities $h00$, $0k0$ and $00l$ be obtained, namely (Fig. 1),

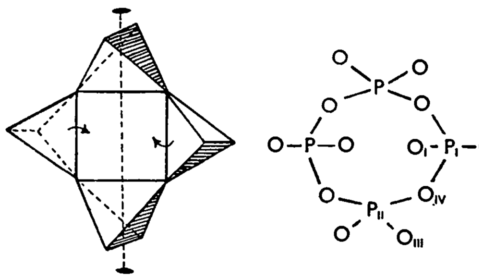
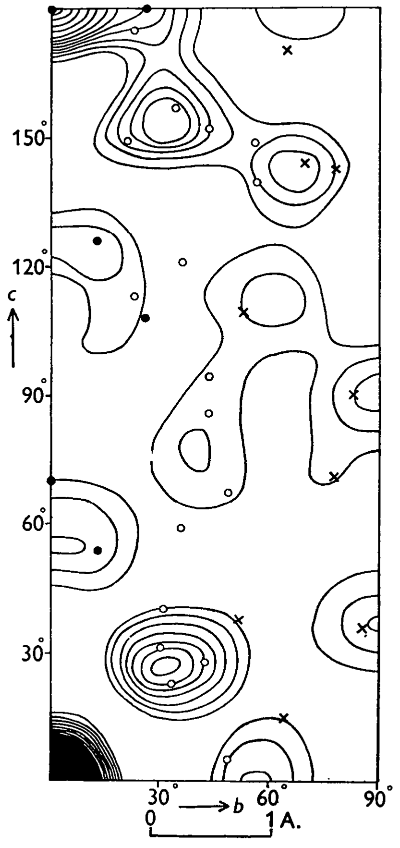


Fig. 1. Position of the complex anion P_4O_{12} with respect to the symmetry elements 2 and m of the space group *Cmca*.

with P_I, O_I and O_{II} in the symmetry plane (position $8f$), with the twofold axis running through P_{II}, and with O_{III} and O_{IV} in general positions $16g$.

Assuming the tetrahedra to be regular and the phosphorus atoms to be in their centres of gravity, our model has two degrees of freedom: (1) simultaneous rotation of the two tetrahedra P_I about their edges O_{IV}–O_{IV}, (2) rotation of the whole anion about the twofold axis. The first rotation is restricted on geometrical grounds. It is assumed that O_I can approach those O_{IV} atoms which do not belong to the same tetrahedron as O_I to a distance not less than 3 A.; the plane O_{IV}–P_I–$O_{IV'}$ then includes an angle of 75° with the plane of the four O_{IV} atoms. Assuming this to be the correct shape of the anion, the dependence of the structure factors $0k0$ on the rotation about the twofold axis was investigated, and the best fit was found when the plane of the four O_{IV} atoms included an angle of 50° with the plane (001). It must be remarked that only a rough agreement was obtained in this way. This is partly due to the circumstance that during this stage of the investigation it was impossible to determine the positions of the ammonium ions, which were accordingly left out in the calculation.



• P–P vectors ○ P–O vectors × P–NH_4 vectors

Fig. 2. Vector map $P(y, z)$.

4. Refinement from vector maps

To test the model and, possibly, find the NH_4 ions, Patterson projections along [110], [100] and [010] were computed. Intensities *hhl*, *0kl* and *h0l* were estimated visually and corrected for Lorentz and polarization factors. Absorption was negligible on the Mo *K* photographs used. Of these vector maps, only one (Fig. 2) is given here. For the others, the reader is referred to the thesis of one of us (Romers, 1948). The maps confirmed the general picture of the structure; there were only few indications of P–NH_4 distances. It turned out that one-half of the ammonium ions is placed in the eightfold position 8*e*, that is, on the twofold axis $\frac{1}{4}, y, \frac{1}{4}$, etc. The co-ordinates derived from the vector maps are shown in Table 1.

Table 1. *Atomic co-ordinates (in degrees) derived from Patterson maps*

	x	*y*	*z*
P_I	0	10	55
P_{II}	75	0	0
O_I	0	−45	55
O_{II}	0	40	85
O_{III}	105	−30	30
O_{IV}	45	30	30
$(NH_4)_I$	90	105	90

5. Refinement by Fourier synthesis

With the aid of these co-ordinates two-dimensional Fourier syntheses were made along [100], [110] (Fig. 3(*a*)), and [010] (Fig. 4(*a*)). The projection along [100] showed all atoms clearly resolved save O_{II} at 0, 43, 85° which is overlapped by a second O_{II} at 180, 43, 180–85°. $(NH_4)_I$ is indeed found in position 8*e* with $y = 98°$, and $(NH_4)_{II}$ with $y = 112°$ and $z = -16°$, must then be in 8*f*.

The direction [110] was chosen for the second projection because it is the shortest translation in the lattice, which is centred in the plane 001. This projection has an additional advantage: owing to the partial loss of symmetry in this projection, two asymmetric units project in different ways. In principle, therefore, *all* atomic co-ordinates can be determined from this one projection (MacGillavry, Hoogschagen & Sixma, 1948). Unfortunately, in the present case there was partial overlap of the atoms O_{III} and O_{IV} in general position, but the three co-ordinates of practically all the other atoms could be found from the projection [110]. In particular, the *z* co-ordinate of O_{II} and the *x* value of O_{IV} (the latter by making use of the *y* value found in the [100] projection) could be evaluated from this map. Finally, the *x* co-ordinate of O_{III} was found from the electron-density map [010]. The results from the three maps are compared in Table 2.

Table 2. *Atomic co-ordinates (in degrees) derived from the Fourier maps*

	[100]		[110]			[010]	
	y	*z*	*x*	*y*	*z*	*x*	*z*
P_I	13	54	0	12	54	0	(55)
P_{II}	0	0	76	0	0	76	0
O_I	−36	59	0	−37½	58	0	(55)
O_{II}	43½	(90)	0	43½	85	0	90
O_{III}	−34½	22	(97)	−34*	23	102	23
O_{IV}	28	27½	44	28*	28	43	26½
$(NH_4)_I$	98	90	90	(105)	90	90	90
$(NH_4)_{II}$	112½	−15½	0	115	−15	0	−16

* These *y* values have been taken from the [100] projection. Values in brackets are uncertain.

6. Estimate of errors

In order to obtain an impression of the accuracy of the co-ordinates, the possible deviations in the atomic positions, as caused by uncertainties in the measured intensities, were calculated using Booth's method (Booth, 1947 *a*, *b*). The experimental errors in $|F|$ were estimated by comparison of the three series of values for $F(00l)$, as found from the Weissenberg diagrams $0kl$, $h\bar{h}l$ and $h0l$ respectively. The phosphorus co-ordinates turned out to be accurate to 0·02 A., the oxygen and ammonium co-ordinates to 0·04 A.

The electron-density maps were calculated with Beevers–Lipson strips, in steps of 6° and to two significant figures. The influence of errors caused by this method of calculation was estimated by Booth's differential analysis (Booth, 1946). These deviations are found to be small compared with those caused by errors in the intensities, save for $(NH_4)_{II}$. The deviations in this case, $\Delta y = 0{\cdot}089$, $\Delta z = -0{\cdot}032$ A., are large, probably because the peaks of this ion in the electron-density maps were low and flat, making it difficult to locate the maximum. For details of the error calculation, see Romers (1948).

The co-ordinates finally adopted are given in Table 3.

Calculated and observed F's are given in Table 4.

Table 3. *Final atomic co-ordinates in fractions of cell edge**

	x	y	z
P_I	0	$0{\cdot}036 \pm 0{\cdot}002$	$0{\cdot}150 \pm 0{\cdot}002$
P_{II}	$0{\cdot}211 \pm 0{\cdot}002$	0	0
O_I	0	$-0{\cdot}100 \pm 0{\cdot}004$	$0{\cdot}164 \pm 0{\cdot}003$
O_{II}	0	$0{\cdot}121 \pm 0{\cdot}004$	$0{\cdot}236 \pm 0{\cdot}003$
O_{III}	$0{\cdot}283 \pm 0{\cdot}004$	$-0{\cdot}095 \pm 0{\cdot}004$	$0{\cdot}064 \pm 0{\cdot}003$
O_{IV}	$0{\cdot}120 \pm 0{\cdot}004$	$0{\cdot}078 \pm 0{\cdot}004$	$0{\cdot}075 \pm 0{\cdot}003$
$(NH_4)_I$	0·250	$0{\cdot}272 \pm 0{\cdot}004$	0·250
$(NH_4)_{II}$	0	$0{\cdot}319 \pm 0{\cdot}004$	$-0{\cdot}044 \pm 0{\cdot}003$

* In a preliminary communication (Romers, MacGillavry & Ketelaar, 1949) the limits of error of the phosphorus atoms were erroneously given ten times too large.

Table 4. *Comparison of $F_{calc.}$ and $F_{obs.}$ for reflexions $0hl$, hhl and $h0l$*

Intensity data from Mo*K* films, except those marked with asterisk which were derived from Cu*K* films. The latter reflexions either occurred at too low θ to be registered on Mo films, or were lost in the background. No correction for temperature movement has been made. Each set of reflexions is arranged in order of increasing θ.

hkl	$F_{calc.}$	$\|F_{obs.}\|$	*hkl*	$F_{calc.}$	$\|F_{obs.}\|$	*hkl*	$F_{calc.}$	$\|F_{obs.}\|$
002	17	17*	068	15	14	0,8,12	5	7
020	26	25*	0,4,10	7	6	0,12,6	− 1·6	—
021	− 5	7*	086	7	8	0,10,10	5	7
022	18	17	0,2,11	0·5	—	0,6,14	1	—
022	− 1	—	069	− 1·5	—	0,0,16	5	4
003	11	10	087	− 6	7	0,8,13	3	—
004	− 8	8	0,10,0	11	11	0,2,16	3	—
040	− 1	1	0,10,1	− 4	4	0,6,14	− 6	8
041	− 8	9	0,10,2	11	12	0,14,0	− 1	—
042	2	4	0,4,11	5	4	0,14,1	3	—
025	− 5	7	0,0,12	17	18	0,14,2	8	6
043	2	—	0,10,3	3	1	0,12,9	− 5	6
006	− 4	5*	0,6,10	9	10	0,14,3	− 0·6	—
044	7	7	0,2,12	11	11	0,10,12	− 4	5
026	14	13	088	11	11	0,8,14	− 1	—
045	5	7	0,10,4	9	11	0,14,4	8	8
060	− 9	11	0,10,5	7	12	0,14,6	− 1	3
061	− 5	7	0,4,12	5	6	0,12,10	9	9
062	5	8	089	− 7	9	0,14,7	1	3
027	5	9	0,6,11	7	6	0,0,18	5	4
046	18	16	0,2,13	− 1	—	0,8,16	5	5
063	−14	14	0,10,6	1	—	0,12,12	5	4
008	0·2	0·5*	0,13,7	− 1	2	0,16,2	3	4
064	11	11	0,8,10	6	4	0,10,15	− 1	4
028	3	2	0,4,13	− 0·4	—	0,16,4	9	5
047	6	7	0,6,12	0·3	—	0,14,10	11	10
065	10	12	0,0,14	15	13	0,10,16	8	4
066	19	19	0,12,0	6	5	0,0,20	5	9
029	− 2	3	0,2,14	14	16	0,4,20	9	4
080	5	4	0,12,1	− 0·3	—	0,6,20	8	4
081	−10	13	0,10,8	0	—	0,12,16	8	2
082	0	—	0,12,2	13	14	0,16,10	10	6
083	− 4	2	0,12,3	4	1	0,18,4	7	2
067	−11	10	0,8,11	8	9	0,14,16	6	3
048	15	14	0,12,4	7	7			
0,0,10	−11	16	0,4,14	7	7	111	18	21*
049	− 2	1	0,6,13	4	4	002	17	16*
084	12	12	0,10,9	− 8	6	113	−16	17*
0,2,10	1	1	0,12,5	2	—	221	−13	16*
085	6	9	0,2,15	− 4	2	222	−28	27*

Table 4. (*cont.*)

hkl	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	*hkl*	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$	*hkl*	$F_{\text{calc.}}$	$\lvert F_{\text{obs.}} \rvert$
004	11	10*	0,0,14	14	14	0,0,10	−11	13
223	− 8	8*	6,6,10	− 2	5	800	19	19
224	−13	16*	778	− 8	8	2,0,10	−14	14
332	7	10*	885	9	9	8,0,22	− 7	7
333	− 9	12*	779	− 2	4	804	− 7	7
006	− 4	4*	5,5,12	4	4	608	3	—
225	−17	17	6,6,11	4	4	4,0,10	−12	14
334	9	12	991	1	3	806	− 2	—
440	4	5	5,5,13	9	10	0,0,12	17	16
442	4	6	7,7,10	4	4	2,0,12	− 3	—
335	− 6	7	4,4,14	6	8	6,0,10	− 9	10
117	8	10	993	5	3	10,0,0	20	19
443	13	15	994	9	7	10,0,2	4	8
336	5	6	0,0,16	3	4	808	− 2	—
008	0·3	1*	995	7	6	4,0,12	6	6
118	5	7	2,2,16	−10	7	10,0,4	− 1·5	—
445	13	13	889	− 7	8	0,0,14	15	13
551	13	14	7,7,12	6	6	10,0,6	8	9
552	− 5	6	5,5,15	11	11	6,0,12	2	3
553	9	9	2,2,13	4	3	8,0,10	−12	12
446	7	8	2,2,14	− 2	3	2,0,14	− 4	3
119	− 4	6	777	− 3	3	4,0,14	2	—
554	− 3	5	992	− 2	2	10,0,8	3	—
229	3	3	996	5	3	12,0,0	− 1	—
338	− 3	6	7,7,11	− 5	8	12,0,2	−14	16
0,0,10	−11	10	997	5	5	12,0,4	− 8	7
660	4	5	998	− 7	6	8,0,12	4	3
661	− 6	8	8,8,11	3	6	6,0,14	1	—
339	− 9	11	7,7,13	− 7	7	0,0,16	5	5
556	4	5	3,3,17	− 8	7	10,0,10	− 4	3
448	7	7	999	7	5	12,0,6	4	—
2,2,10	−16	16	0,0,18	4	4	2,0,16	−11	11
663	− 3	3	0,9,10	− 4	5	4,0,16	− 1	—
557	4	4	2,2,18	− 6	6	12,0,8	2	—
3,3,10	− 9	10	3,3,18	4	4	2,0,14	3	—
449	−10	10	7,7,15	− 7	7	10,0,12	8	5
665	10	10	5,5,18	6	4	14,0,0	15	16
2,2,11	6	8	0,0,20	5	9	6,0,16	− 7	6
558	− 9	10				14,0,2	3	5
666	− 4	4	002	17	16*	0,0,18	5	4
771	−11	11	200	4	5*	14,0,4	1	—
0,0,12	17	17	202	−16	19*	2,0,18	− 5	—
772	−10	11	004	11	14*	12,0,10	−10	13
1,1,12	4	3	304	−19	20	14,0,6	8	8
3,3,11	− 8	11	400	36	38	10,0,14	8	4
773	− 7	9	402	− 7	7	12,0,12	− 3	3
667	− 5	5	006	− 4	4*	4,0,18	5	—
774	7	5	206	10	10	0,0,20	5	9
1,1,13	13	13	404	8	8	2,0,20	0	—
775	− 4	3	406	12	10	16,0,0	4	—
776	4	5	600	12	11	16,0,2	− 7	3
880	− 4	4	602	− 6	7	16,0,4	− 6	—
881	− 5	8	008	0·2	0·5*	4,0,20	9	5
882	− 7	7	208	− 1	—	18,0,0	11	7
4,4,12	4	6	604	− 7	7			
669	− 5	7	606	11	9			
5,5,11	5	7	408	10	13			

7. Discussion of the structure

The structure consists of tetramer ring-shaped anions P_4O_{12} and NH_4 ions (Figs. 3 (*b*), 4 (*b*)). The anions are rather flat and nearly parallel to (010). This is in agreement with the fact that light vibrating in the direction of the *b* axis has the smallest refractive index. The crystals show no cleavage parallel to (010); this is also evident from the crystal structure. The layers of P_4O_{12} anions, whose centres lie at 0,0,0, $\frac{1}{2},0,\frac{1}{2}$, and $0,\frac{1}{2},\frac{1}{2}$, $\frac{1}{2},\frac{1}{2},0$ respectively, are interleaved by layers of NH_4 ions at y = approximately $\frac{1}{4}$ and $\frac{3}{4}$. In such a layer the NH_4 ions are roughly packed in a centred mesh with repeat units $\frac{1}{2}a$ and $\frac{1}{2}c$ (see Fig. 4 (*b*)). This sandwich-like packing of alternate positive and negative layers parallel to (010) gives strong cohesion.

The interatomic distances show some interesting features. Those inside the PO_4 tetrahedra are given in Table 5 and some of the bond angles in Table 6. The following facts are seen from these tables:

Table 5. *Distances* P–O *and* O–O *inside* PO_4 *tetrahedra*

P_I–O_I	1·48 A.	O_I–O_{II}	2·56 A.
P_I–O_{II}	1·44 A.	O_{III}–O_{III}	2·60 A.
P_I–O_{IV}	1·63 A. (2 ×)	O_{III}–O_{IV}	2·52 A. (2 ×)
P_{II}–O_{IV}	1·59 A. (2 ×)	O_{IV}–O_{III}	2·46 A. (2 ×)
P_{II}–O_{III}	1·51 A. (2 ×)	O_{IV}–O_{IV}	2·49 A. (2 ×) 2·52 A. (2 ×)
		O_{IV}–O_I	2·55 A. (2 ×)
		O_{IV}–O_{II}	2·44 A. (2 ×)

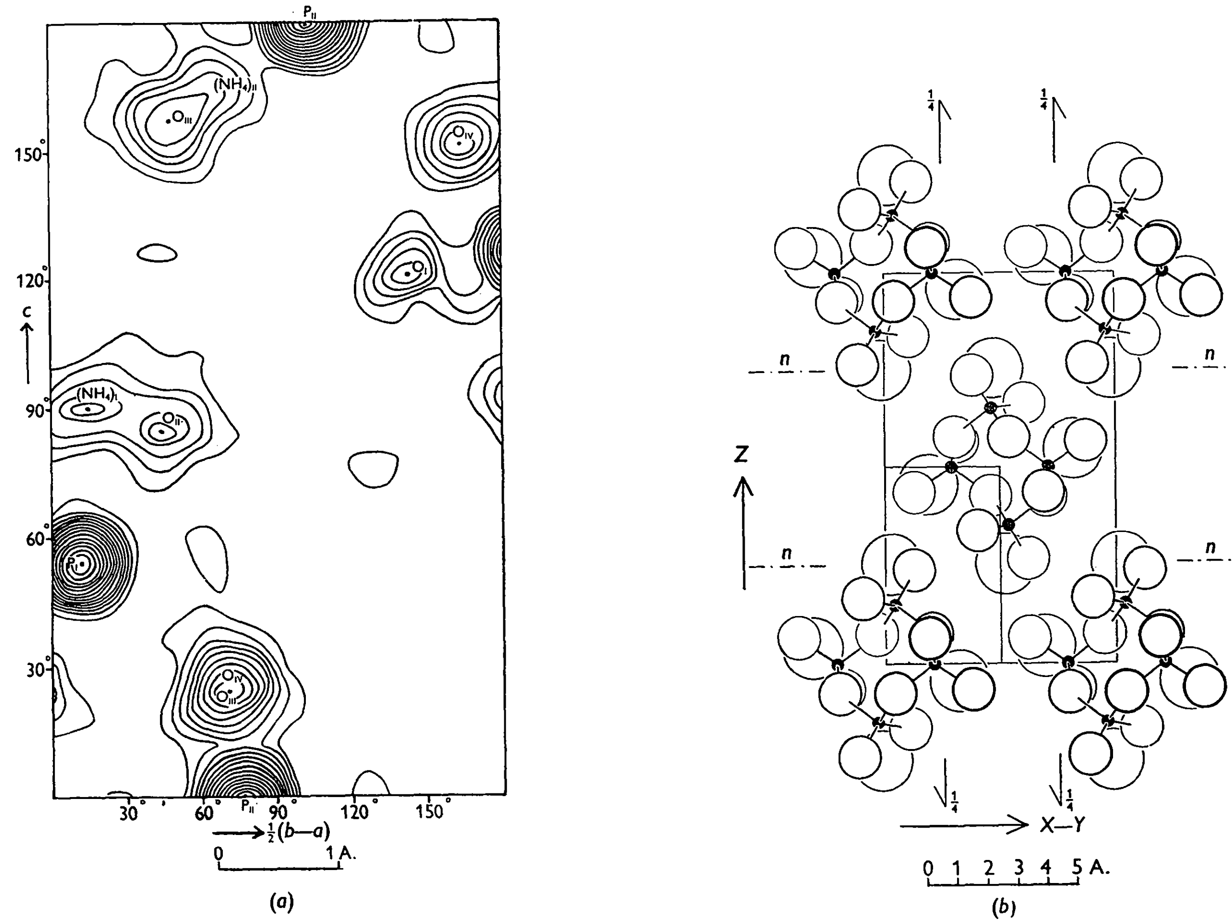


Fig. 3. (a) Electron density projected along [110]. (b) Atomic positions viewed along [110]. The part of the cell corresponding to (a) is indicated.

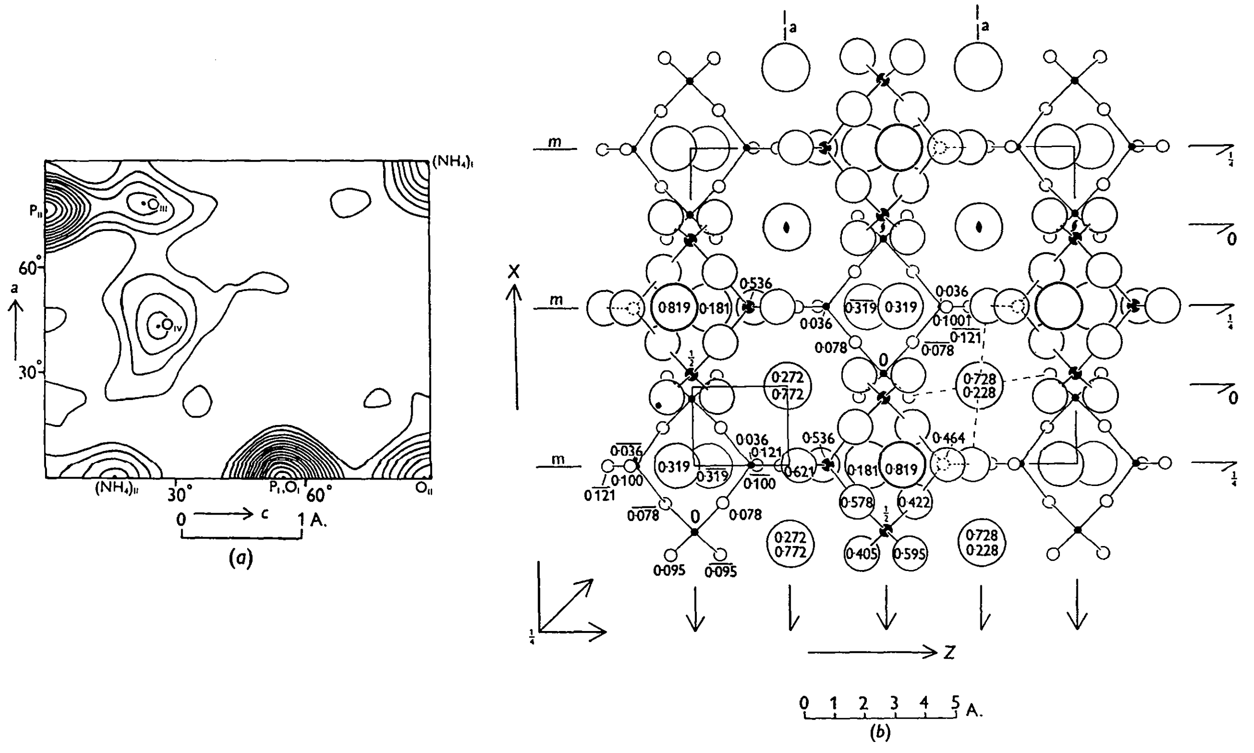


Fig. 4. (a) Electron density projected along the b axis. (b) Atomic positions viewed along the b axis. For clarity the P and O atoms lying at a lower level have been drawn smaller than those at higher level. Hydrogen bridges formed by $(NH_4)_I$ are indicated by dot-dash lines. The part of the cell corresponding to (a) is indicated.

Table 6. *Bond angles*

$\mathrm{P_I{-}O_{IV}{-}P_{II}}$	132°
$\mathrm{O_I{-}P_I{-}O_{II}}$	122°
$\mathrm{O_{III}{-}P_{II}{-}O_{III}}$	120°
$\mathrm{O_{IV}{-}P_I{-}O_{IV}}$	100°
$\mathrm{O_{IV}{-}P_{II}{-}O_{IV}}$	110°

(1) The oxygen tetrahedra are, within the limits of error, regular with edge 2·51 A. The somewhat larger distances $\mathrm{O_I{-}O_{II}}$ and $\mathrm{O_{III}{-}O_{III}}$ may or may not be significant (see below).

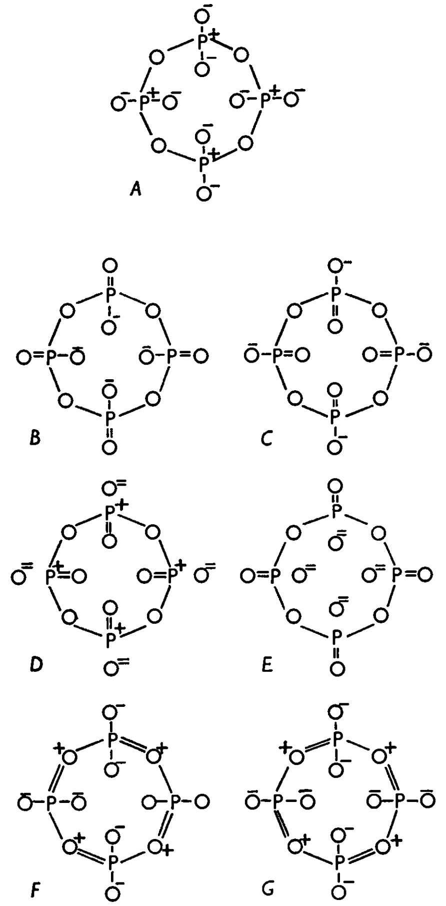


Fig. 5. Covalent bond systems theoretically possible in a $\mathrm{P_4O_{12}^{4-}}$ ion with ring structure.

(2) The phosphorus atoms are not in the centres of these tetrahedra, but are shifted away from the oxygen atoms common to two tetrahedra ($\mathrm{O_{IV}}$). The same effect was found in the three modifications of phosphorus pentoxide (de Decker & MacGillavry, 1941; de Decker, 1941; MacGillavry, Nijland & de Decker, 1949), and in sulphur trioxide (Westrik & MacGillavry, 1941). The valence angle of the ring oxygen is large; those of the phosphorus deviate markedly from the tetrahedron angle. It is possible to 'explain' these effects if the bonds are considered to be chiefly electrostatic bonds between $\mathrm{O^{2-}}$ and $\mathrm{P^{5+}}$ ions: the mutual repulsion between the central P ions would then enlarge the valence angle of $\mathrm{O_{IV}}$ and the distances $\mathrm{P{-}O_{IV}}$. However, the electron-density maps show that phosphorus contains about twice as many electrons as oxygen. Since the ratio of electrons in $\mathrm{P^{5+}}$ and $\mathrm{O^{2-}}$ is 10/10, and 15/8 in neutral P and O, the conclusion must be drawn that the bonds are chiefly homopolar in nature. (This was also found in the three forms of phosphorus pentoxide.) The cause of the great variety of bond lengths P–O and S–O is still uncertain (Wells, 1949). It is possible to conceive a number of resonance structures, as in Fig. 5, amongst which structure *A* would be prominent.

Besides *A* the equivalent configurations *B* and *C* as well as *D* and *E* will most probably contribute appreciably to the stationary state, thus decreasing the bond distances of the phosphorus atom to $\mathrm{O_I}$, $\mathrm{O_{II}}$ and $\mathrm{O_{III}}$ in contrast with the longer P–O distances in the ring (cf. Pauling, 1945, p. 241).

Also, a change in the hybridization ratio might very well cause a deviation of the bond angles from the tetrahedral values. The large angles $\mathrm{O_I{-}P_I{-}O_{II}}$ and $\mathrm{O_{III}{-}P{-}O_{III}}$ of 122 and 120° respectively are in accordance both with a double-bond character of these P–O bonds and with a preponderance of *s* character. The latter circumstance might also cause a decrease of the bond distance as observed.

Another point of interest is revealed by the surrounding of the $\mathrm{NH_4}$ ions. The following N...O distances are found:

$\mathrm{(NH_4)_I}$ to	$\mathrm{O_{III}}$	2·79 A. (2×)
	$\mathrm{O_{II}}$	3·03 A. (2×)
	$\mathrm{O_I}$	3·14 A. (2×)
	$\mathrm{O_{IV}}$	3·38 A. (2×)
$\mathrm{(NH_4)_{II}}$ to	$\mathrm{O_I}$	2·80 A.
	$\mathrm{O_{II}}$	2·85 A.
	$\mathrm{O_{III}}$	2·82 A. (2×)
	$\mathrm{O_{IV}}$	3·25 A. (2×)

Thus, both ammonium ions have four nearest neighbours which in both cases are arranged in a deformed tetrahedron, namely, two $\mathrm{O_{III}}$ and $\mathrm{O_{II}}$ each in the case of $\mathrm{(NH_4)_I}$ and one $\mathrm{O_I}$, one $\mathrm{O_{II}}$ and two $\mathrm{O_{III}}$ in the case of $\mathrm{(NH_4)_{II}}$. This surrounding very strongly suggests the presence of hydrogen bridges N–H...O. It may be mentioned that such bridges of length 2·8 A. have been reported in several other cases. $\mathrm{O_{III}}$ has two ingoing hydrogen bridges under an angle of roughly 120°. $\mathrm{O_I}$ apparently forms only one bridge; $\mathrm{O_{II}}$, however, has three. It is remarkable that the ring oxygen $\mathrm{O_{IV}}$, which is bound to two phosphorus atoms and is therefore less electronegative, shows no tendency to come close to any of the $\mathrm{NH_4}$ groups.

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Structure Cristalline de l'Acide Nitrique Anhydre

PAR V. LUZZATI

Laboratoire Central des Services Chimiques de l'État, 12 *Quai Henri IV, Paris IV, France*

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Anhydrous HNO_3 crystallizes at $-41{\cdot}6°$ C. Bouttier's method has been used for the preparation and the transport of the crystals, and Weissenberg diagrams of several layer lines have been obtained, using rotation about the three crystallographic axes. The unit cell is given by the three orthogonal translations $a = 16{\cdot}23$, $b = 8{\cdot}57$, $c = 6{\cdot}31$ A., and contains 16 molecules NHO_3. The group of symmetry is $P2_1/a$–C^5_{2h} in the monoclinic system, with $\beta = 90°$. The crystals obtained showed submicroscopic twinning. The atomic parameters were obtained from three projections of the electron density.

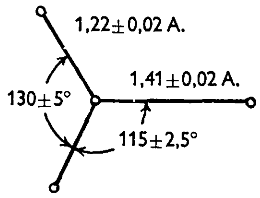
Continuous streaks are observed along some lines in the reciprocal lattice. An interpretation of these in terms of a certain disorder in the structure is suggested.

Introduction

Ce travail forme partie d'une étude entreprise dans ce laboratoire sur la structure cristalline de l'acide nitrique et de quelques composés similaires. Une première structure, celle de N_2O_5, a été déterminée par Grison, Eriks & de Vries (1950); d'autre part nous même nous occupons des $HNO_3.H_2O$ et $HNO_3.3H_2O$ (Luzzati, 1950).

La structure de la molécule de HNO_3 a fait l'objet de plusieurs études. Par l'interprétation des spectres Raman de HNO_3 anhydre liquide, Chedin (1939) a déterminé que la molécule possède la symétrie *mm*.

Maxwell & Mosley (1940) ont déterminé la structure de la molécule de HNO_3 gazeux par la diffraction d'électrons, et ont proposé la forme suivante:



Bauer & Magat (1944), considérant des modèles électrostatiques, et par des calculs d'énergie potentielle, ont discuté les associations possibles des molécules HNO_3 dans le cristal, et ils ont conclu que chaque molécule doit être entourée par plusieurs molécules voisines, trois au minimum, et qu'il n'y a pas formation de dimères, comme Dalmon & Freymann l'avaient suggéré (1940).

L'intérêt de la détermination de la structure cristalline de l'acide nitrique nous a paru certain, spécialement si l'étude pouvait être étendue aux hydrates et à quelques composés similaires.

La collaboration avec M. L. Bouttier nous a permis d'utiliser l'appareil qu'il a fabriqué pour la production de cristaux à basse température (Bouttier, 1949), et avec lui nous avons mis au point une technique pour la manipulation des cristaux.

Partie expérimentale

L'acide nitrique anhydre cristallise à $-41{,}6°$ C. Nous avons utilisé toujours des cristaux uniques, de préférence avec des formes régulières, dont le volume était 2–3 mm.^{3} au maximum. Les cristaux qui adhèrent sur un fil d'aluminium croissent rarement en conservant des faces et des arêtes bien définies, et très souvent il a fallu effectuer le réglage des cristaux au moyen des rayons X. Nous avons réglé les cristaux et nous les avons conservés dans la chambre de Weissenberg sous un jet d'air froid et sec, provenant de l'évaporation d'air liquide.

Nous avons enregistré les diagrammes de Weissenberg des trois équateurs et de plusieurs strates. Les conditions expérimentales étaient telles qu'en deux