

## Hydrogen Bonding in the Crystalline State. Crystal Structure and Twinning of $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (Stercorite)

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(Received 15 October 1973; accepted 17 October 1973)

Sodium ammonium hydrogen phosphate tetrahydrate ( $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , stercorite) crystallizes in the space group  $P\bar{1}$  with  $a = 10.636$  (2),  $b = 6.9187$  (14),  $c = 6.4359$  (13) Å,  $\alpha = 90.46$  (3),  $\beta = 97.87$  (3),  $\gamma = 109.20$  (3)°,  $Z = 2$ . The structure was solved by direct methods and refined anisotropically ( $R = 0.087$ ) with 1582 reflexions collected from a twinned crystal on a diffractometer (Cu  $K\alpha$  radiation). Corrections for absorption and anomalous scattering were applied.  $C2/m$  pseudo-symmetry, which accounts for easy  $\{010\}$  twinning, is obeyed by nearly the whole structure with the exception of the two positions occupied by a water molecule and  $\text{NH}_4^+$  respectively. A (100) layered structure is built up by  $[010]$  rows of Na octahedra sandwiched between P tetrahedra;  $\text{NH}_4^+$  and its pseudo-equivalent water molecule, which have tetrahedral environments, intercalate the layers and link them through hydrogen bonds. The bond strengths and the geometry of the tetrahedral anion are discussed.

### Introduction

Sodium ammonium hydrogen phosphate tetrahydrate ( $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ ), a compound used in blowpipe analysis, is present in human urine (microcosmic salt; Pascal, 1956) and corresponds (Ferraris & Franchini-Angela, 1974) to the mineral stercorite found in guano deposits (Palache, Berman & Frondel, 1963). It is isostructural with  $\text{NaNH}_4\text{HAsO}_4 \cdot 4\text{H}_2\text{O}$ ; both are triclinic but their crystals are always  $\{010\}$  twinned because of a marked pseudo-monoclinic symmetry of the individuals (Ferraris & Franchini-Angela, 1974).

A crystal structure determination of the phosphate, which is more stable than the arsenate, has been carried out with the aim of solving the problem of the twinning and as part of a programme of research on hydrogen bonding and on the role of the water molecule in the crystalline state [last paper in the series is Catti & Ferraris (1974)].

### Experimental

#### Crystal data

Vitreous, colourless crystals of  $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  are commercially available: they are prismatic  $[001]$  and deteriorate in air.

The split of several reflexions on  $[001]$  Weissenberg photographs (Cu  $K\alpha$  radiation) proved that all the available crystals were  $\{010\}$  twinned, and that the symmetry of the individuals was actually primitive triclinic but apparently  $C2/m$ . The reciprocal unit-cell parameters were obtained by least-squares refinement from 29  $\theta$  values of split reflexions ( $\theta > 63^\circ$ ,  $\lambda_1 = 1.5405$  Å) which were measured on a diffractometer. The values of the direct unit-cell parameters are (estimated standard deviations in parentheses):  $a = 10.636$  (2),  $b = 6.9187$  (14),  $c = 6.4359$  (13) Å,  $\alpha = 90.46$  (3),  $\beta = 97.87$  (3),  $\gamma = 109.20$  (3)°; the  $C$  pseudo-monoclinic unit

cell has the same  $b$ ,  $c$  and  $\alpha$  values and  $a = 20.090$  (3) Å,  $\beta = 98.50$  (3),  $\gamma = 90.22$  (2)°. The transformation matrix from the former to the latter cell is 210/010/001.

Other physical data are: space group  $P\bar{1}$ , M.W. 209.078,  $V = 442.64$  Å<sup>3</sup>,  $D_m = 1.574$  (Schaschek, 1914),  $D_c = 1.570$  g cm<sup>-3</sup>,  $Z = 2$ ,  $F(000) = 220$ ,  $\mu = 34.3$  cm<sup>-1</sup> for Cu  $K\alpha$ .

#### Intensity measurements

Integrated intensities were measured by a General Electric automatic three-circle diffractometer [ $\theta$ - $2\theta$  scanning, 1° min<sup>-1</sup>, 0.4° background on both sides of each peak, a standard reflexion ( $\bar{4}22$ ) periodically checked] from a twin mounted with its  $z$  axis along the instrumental  $\varphi$  axis and coated with a thin plasticizing film. On the basis of the instrumental coordinates,\* the accessible reflexions were divided into two groups with some repetitions: (i) unsplit reflexions (1154), the contribution from the whole twin was measured; (ii) split reflexions (875), the intensity arising from the larger of the two differently oriented parts of the twin was measured. The degree of overlap of the reflexions was larger for the  $hkl$  and  $\bar{h}\bar{k}l$  octants and reflexions related by the twin symmetry showed quite similar intensities.

An absorption correction (0.66–0.79 for  $|F_o|$ ) was applied by the program *GONO9* (Hamilton, 1966); the twinning undoubtedly lowers the standard of such a correction for which the following dimensions of the slightly idealized crystal were used: 0.17, 0.20 and 0.36 mm across the opposite faces of  $\{100\}$ ,  $\{010\}$  and  $\{001\}$  respectively. Atomic scattering factors, including  $\Delta f'$  and  $\Delta f''$ , were linear interpolations of the values reported for neutral atoms in *International Tables for X-ray Crystallography* (1962).

\* The  $C$  pseudo-monoclinic unit cell has been used as reference system in the experimental section.

*The unique set of reflexions*

It is known (Huml, 1967; Britton, 1972) that it is possible to obtain the intensities scattered by a single crystal from intensities measured on a twin provided (a) the two parts of the twin have significantly different volumes, (b) the individual and the twin have substantially different symmetries. If (a) or/and (b) are not reasonably satisfied, the pseudo-equivalent intensities  $I_1$  and  $I_2$  of the twin are 'equal'.

On the basis of the inequality (Huml, 1967)

$$0 \leq v \leq \frac{I_1}{I_1 + I_2}$$

and of the ratio between the measured intensities of pairs of identical reflexions (mainly  $00l$  and  $h0l$ ) belonging to the two different parts of the twin, the fractional volume  $v$  of the smaller was about 0.45 of the whole crystal. At this stage the small difference between  $I_1$  and  $I_2$  could be ascribed both to (a) or/and (b), as well as, at least in part, to experimental errors. Application to the unsplit reflexions of known procedures (Huml, 1967; Britton, 1972) supplied a set of approximate intensities which were roughly put on the same scale as the intensities measured from an individual. These intensities permitted the solution and a moderate refinement of the crystal structure; afterwards it turned out that (b) was fairly well satisfied.

Therefore, after rejection of weak unreliable reflexions ( $|F_c|$  consistently less than  $|F_o|$ ), a unique set of 1582 reflexions referred to the triclinic  $P$  unit cell was obtained by the union, with two different scale factors, of the reflexions containing the contribution of the whole twin to those measured from an individual.\*

**Structure analysis***Solution and refinement of the structure*

Statistical tests indicated centrosymmetry and the crystal structure was solved in the space group  $P\bar{1}$  by direct methods with the 200 largest  $|E|$ 's ( $> 1.47$ ) and the program *MULTAN* (Germain, Main & Woolfson, 1971); the  $E$  map corresponding to the solution with the highest 'combined' figure of merit showed all the P, Na, O and N atoms. A least-squares refinement was started with isotropic temperature factors and was completed, anisotropically, when all the shifts were less than the estimated standard deviations. The full-matrix least-squares program by Busing, Martin & Levy (1962), with minor modifications, and in the later

\* A list of  $|F_o|$  and  $F_c$  has been deposited with the British Library Lending Division, as Supplementary Publication No. 30248 (7 pp.). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates ( $\times 10^4$ ) and vibrational parameters ( $\text{\AA}^2 \times 10^2$ ) with significant figures of e.s.d.'s in parentheses*

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
P	7314 (1)	3656 (1)	4425 (2)	157 (4)	141 (4)	215 (4)	52 (3)	89 (3)	45 (3)
Na	5317 (2)	7661 (2)	342 (3)	259 (7)	186 (6)	322 (8)	78 (5)	112 (6)	52 (5)
O(1)	8075 (3)	4044 (5)	2530 (5)	171 (10)	218 (11)	265 (12)	47 (8)	113 (9)	52 (9)
O(2)	7581 (3)	5616 (5)	5736 (5)	250 (12)	171 (10)	313 (13)	82 (9)	84 (10)	10 (9)
O(3)	5767 (3)	2878 (5)	3392 (5)	198 (12)	290 (13)	313 (13)	57 (10)	89 (10)	44 (10)
O(4)	7578 (3)	1961 (5)	5716 (5)	272 (13)	187 (11)	323 (13)	90 (9)	95 (10)	87 (10)
W(1)	6134 (3)	8064 (5)	4078 (5)	257 (12)	187 (11)	352 (14)	72 (9)	116 (10)	57 (10)
W(2)	6552 (4)	5619 (5)	-563 (5)	325 (14)	301 (14)	317 (14)	161 (11)	146 (11)	75 (11)
W(3)	6557 (4)	936 (5)	-570 (5)	312 (14)	214 (12)	310 (13)	45 (10)	139 (11)	52 (10)
W(4)	-28 (4)	7903 (6)	2265 (7)	306 (15)	313 (15)	447 (18)	77 (12)	72 (13)	104 (13)
N	-46 (4)	2048 (6)	2199 (7)	243 (14)	273 (15)	369 (17)	132 (12)	85 (13)	1 (13)

Table 2. *Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) involving the water molecules*

An arrow departs from the donor of a hydrogen bond:  $A'$  and  $C'$  indicate the atoms on the lower line. E.s.d.'s are 0.005  $\text{\AA}$  for the distances and 0.2 $^\circ$  for the angles.

	$A$	$B$	$C$	$AB$	$BC$	$\angle ABA'$	$\angle CBC'$
	O(3') <sup>III</sup>	↘	↗				
	Na	↘	↗				
	Na(1') <sup>I</sup>	↘	↗				
	Na	↘	↗				
	Na(1') <sup>V</sup>	↘	↗				
	Na(1') <sup>I</sup>	↘	↗				
	N(1) <sup>II</sup>	↘	↗				
	N(1') <sup>II</sup>	↘	↗				

W(1)	O(4) <sup>II</sup>		2.688	2.744	115.8	105.6
W(2)	O(2)		2.423	2.769		
W(2)	O(1)		2.498	2.844	93.7	107.6
W(2)	O(2) <sup>IV</sup>		2.341	2.755		
W(3)	O(1)		2.343	2.825	93.6	107.7
W(3)	O(4) <sup>IV</sup>		2.508	2.762		
W(4)	O(1) <sup>VI</sup>		2.876	2.791	88.6	110.1
W(4)	O(4') <sup>III</sup>		2.886	2.720		

cycles with the following weighting scheme ( $|F_o|$  on absolute scale), was used:

$$w = \frac{10 + 200(\sin \theta/\lambda)^2}{0.08|F_o|^2 + 4|F_o| + 16} \quad \text{if } |F_o| \geq 8$$

$$w = 0.0375|F_o| + 0.7 \quad \text{if } |F_o| < 8.$$

The constants were chosen so as to obtain a roughly constant average value of  $\sum w\Delta^2$  for amplitudes batched in groups of  $|F_o|$  and of  $(\sin \theta/\lambda)^2$ .

The final values of  $R$ ,  $R_w$  and of the standard error of an observation of unit weight were 0.087, 0.084 and 0.67 respectively. Possibly because of the low accuracy of the experimental data, attempts to introduce the usual (see Catti & Ferraris, 1973) extinction correction were unsuccessful. The final fractional coordinates and the  $B_{ij}$  coefficients of the expression:

$$\exp\left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*\right)$$

are listed in Table 1 with the significant figures of the e.s.d.'s.

#### Ambiguity due to the twinning

The pseudo-symmetry requires equivalence between the position of the water molecule  $W(4)^*$  and that of the ammonium ion (see below). The small difference between the scattering powers of oxygen and nitrogen and the strategy used in the data collection could preclude an unambiguous location of the two groups in the untwinned lattice. The following tests, however, permit confidence in the reported positions of  $W(4)$  and N (Table 1); at the final stage of the least-squares refinement three cycles were calculated with (i)  $W(4)$  and N(*i*) statistically distributed, (ii) in the positions reported in the Table 1 and (iii) in the reversed positions. Configuration (iii) yielded the worst figures of merit and (ii) turned out to be possibly better than (i). The choice of (ii) provides a hydrogen-bonding scheme with O...O and N...O separations in agreement with published average values of O...O (Ferraris & Franchini-Angela, 1972) and of N...O (Khan & Baur, 1972); the latter is slightly but significantly larger than the former. One must, however, bear in mind that a complete exchange between  $\text{NH}_4^+$  and  $W(4)$  would be noticed only by O(2) and O(4) (Tables 2 and 3) which, on the other hand, are pseudo-equivalent (see below).

It was not possible to locate satisfactorily all the hydrogen atoms from difference syntheses; some of them were resolved quite clearly, but for others only a broad positive electron density appeared in the expected positions.

\* Figures in parentheses denote atoms in the asymmetric unit; a prime is appended for atoms in the position  $\bar{x}\bar{y}\bar{z}$ . Roman numerals represent translations: I, +a, +b; II, +b; III, +a, +b, +c; IV, -c; V, -b; VI, -a; VII, +a; VIII, +c.

Table 3. *Interatomic distances and angles around the ammonium group*

E.s.d.'s are 0.005 Å and 0.2° for the distances and the angles respectively.

N...O(1) <sup>VI</sup>	2.806 Å
N...O(2) <sup>III</sup>	2.735
N...W(4) <sup>V</sup>	2.876
N...W(4') <sup>II</sup>	2.886
O(1) <sup>VI</sup> ...N...O(2') <sup>III</sup>	109.7°
O(1) <sup>VI</sup> ...N...W(4) <sup>V</sup>	136.7
O(1) <sup>VI</sup> ...N...W(4') <sup>II</sup>	100.6
O(2') <sup>III</sup> ...N...W(4) <sup>V</sup>	105.1
O(2') <sup>III</sup> ...N...W(4') <sup>II</sup>	109.0
W(4) <sup>V</sup> ...N...W(4') <sup>II</sup>	91.4

## Discussion

### Hydrogen bonding and water environment

Even if the twinning prevented the hydrogen atoms from being clearly located, inspection of bond lengths and angles allowed an unequivocal determination of the hydrogen-bonding scheme. The acidic hydrogen atom, which appeared clearly on difference syntheses, is attached to O(3) and participates in the shortest hydrogen bond of the structure [O(3)...W(1') = 2.688 Å]. The four water molecules form medium or medium-strong hydrogen bonds according to tetrahedral environments (Table 2) and, on the basis of the modified (Ferraris & Franchini-Angela, 1972) classification proposed by Chidambaram, Sequeira & Sikka (1964), the water molecules are of class 2 with  $W(1)$ ,  $W(2)$ ,  $W(3)$  and  $W(4)$  of type G, A, A and E respectively.

All the anionic oxygen atoms are to some extent engaged in hydrogen bonding and only O(3) is also Na-coordinated. In particular, O(1) participates in four hydrogen bonds donated by atoms which form the base of a pyramid of which the phosphorus atom is the apex; O(2) and O(4) are each acceptors of three hydrogen bonds and O(3) is only a donor.

### Bond strengths and coordination polyhedra

Bond strengths, which differ from the expected value 2 v.u. (Pauling's second rule) by a maximum of 12%, and bond lengths in the P tetrahedron are in semi-quantitative agreement with proposed correlations (Baur, 1970; Ferraris & Catti, 1973). Thus, the over-bonded O(3) ( $p$  2.25 v.u.) forms the longest P-O bond and the under-bonded O(2) and O(4) ( $p$  about 1.8 v.u.) are engaged in hydrogen (Tables 2 and 3) and P-O (Table 4) bonds which are shorter than those of O(1) ( $p$  about 2 v.u.). The configuration of the  $(\text{PO}_4\text{H})^{2-}$  group is normal (Table 4) with P-OH longer than P-O distances, O-P-OH angles smaller than the others and with deviations from the respective average values smaller for O-O distances (2%) than for the angles (4%).

Distortions having a greater effect on the angles than on the sides have usually been interpreted in terms of shifts of the central atom within a (nearly) rigid tetrahedron of oxygen atoms (Baur, 1970). Recent studies

on feldspars (Ribbe, Phillips & Gibbs, 1973) and, in general, on  $TO_4$  tetrahedra (Ribbe, 1973; Brown, 1973b) show that the 'rigid-tetrahedron' model is unsatisfactory and that there is a correlation between O-T-O and O-O. A close examination of the arsenates and phosphates studied in this laboratory shows that besides indications that support Baur's (1970) model (see, e.g., Catti & Ferraris, 1974), one can also note short (long) O-O sides facing narrow (wide) O-T-O angles. On the other hand, for the sulphate ion Brown (1973a) associates a 'configuration effect' with the rigid-tetrahedron model; such a composite model should also work for phosphates (Brown, 1973b). In our opinion the proposed models are only first approximations which emphasize some aspects of a more complex and general problem that undoubtedly needs further development.

The 'octahedron' around Na shows a peculiar distortion; the four edges converging on O(3), which is the only anionic oxygen atom coordinated by Na, are among the shortest oxygen-oxygen distances in the polyhedron (Table 5) and are even shorter than the two edges that are common to two Na polyhedra. On the other hand, four of the five longest edges depart from the corner opposite O(3); the 'octahedron' looks, therefore, like a double pyramid. According to the above quoted correlations, which are very poor for  $Na^+$ , O(3) ( $p$  2.25 v.u.) would have the longest Na-O distance in the octahedron; this is not true, however,

Table 4. Interatomic distances and O-P-O angles in the  $PO_4$  group

E.s.d.'s are 0.003 and 0.004 Å for P-O and O-O distances respectively and 0.2° for the angles.

P-O(1)	1.532 Å	
P-O(2)	1.515	
P-O(3)	1.598	
P-O(4)	1.521	
Average	1.541	
O(1)-O(2)	2.521 Å	111.6°
O(1)-O(3)	2.462	103.8
O(1)-O(4)	2.531	112.0
O(2)-O(3)	2.518	108.0
O(2)-O(4)	2.528	112.8
O(3)-O(4)	2.525	108.2
Average	2.514	

even if Na-O(3) is longer than the average Na-O length. Discrepancies of the same type are noted for individual distances from Na to crystallographically equivalent water molecules [ $W(2)$  and  $W(2)^I$ ,  $W(3)^I$  and  $W(3)^{II}$ ] (Table 5); consideration of average distances for  $W(2)$  and  $W(3)$  would yield the expected trend between bond lengths and bond strengths around sodium. A satisfactory bond-strength balance should presumably be obtained by application of empirical bond-strength bond-length curves of the type proposed by Brown & Shannon (1973) for oxides; however, owing to the presence of  $NH_4^+$ , these correlations are not strictly applicable to stercorite.

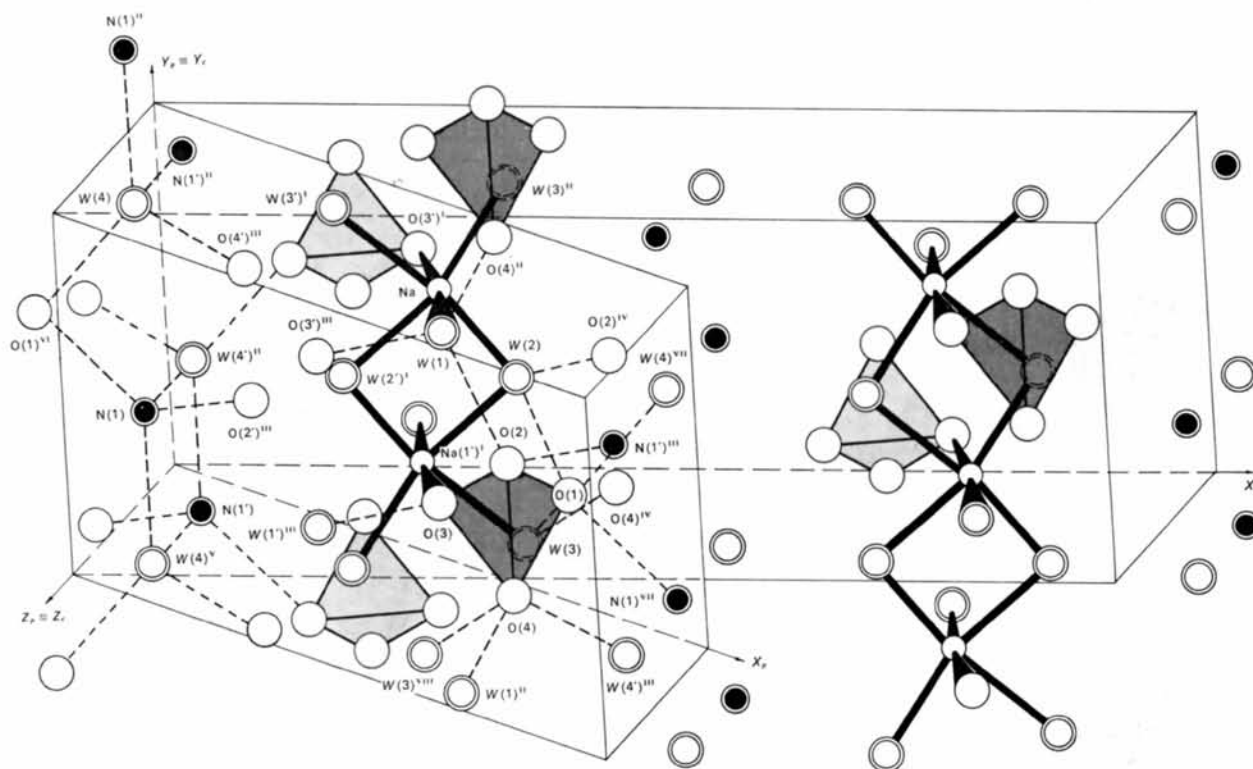


Fig. 1. Primitive ( $P$ ) and centred ( $C$ ) unit cell of stercorite in clinographic projection down  $z$ ; dashed lines show the hydrogen bonds involving atoms of the asymmetric unit.  $W(2)^{VIII}$ , which is donor of a hydrogen bond to O(2), is not shown.

Table 5. Interatomic distances and oxygen–sodium–oxygen angles in the Na coordination polyhedron

E.s.d.'s are 0.004 and 0.005 Å for the sodium–oxygen and oxygen–oxygen distances respectively and  $0.1^\circ$  for the angles.

Na–O(3') <sup>I</sup>	2.488 Å	
Na–W(1)	2.423	
Na–W(2)	2.341	
Na–W(2') <sup>I</sup>	2.498	
Na–W(3) <sup>II</sup>	2.343	
Na–W(3') <sup>I</sup>	2.508	
Average	2.434	
O(3') <sup>I</sup> — W(2)	3.224 Å	86.6°
O(3') <sup>I</sup> — W(2') <sup>I</sup>	3.313	80.6
O(3') <sup>I</sup> — W(3) <sup>II</sup>	3.283	85.6
O(3') <sup>I</sup> — W(3') <sup>I</sup>	3.207	79.9
W(1) — W(2)	3.572	97.1
W(1) — W(2') <sup>I</sup>	3.623	94.8
W(1) — W(3) <sup>II</sup>	3.603	98.2
W(1) — W(3') <sup>I</sup>	3.651	95.5
W(2') <sup>I</sup> — W(3') <sup>I</sup>	3.242	80.7
W(2') <sup>I</sup> — W(2)	3.312	86.3
W(2) — W(3) <sup>II</sup>	3.678	103.5
W(3') <sup>I</sup> — W(3) <sup>II</sup>	3.324	86.5
W(1) ··· O(3') <sup>I</sup>	—	173.9
W(2) ··· W(3') <sup>I</sup>	—	162.6
W(2') <sup>I</sup> ··· W(3) <sup>II</sup>	—	162.5

#### Description of the structure

Stercorite shows clearly (Fig. 1) a (100) layered structure where [010] rows of Na octahedra are sandwiched between P tetrahedra. W(4), (the only water molecule not Na-coordinated) and  $\text{NH}_4^+$  intercalate the layers and hold them together through hydrogen bonds.

Each octahedron shares two edges with its two centrosymmetric neighbours forming  $[\text{Na}(\text{H}_2\text{O})_3\text{OH}]_\infty$  chains, which, in turn, are linked by acidic hydrogen bonds in such a way that an infinite (100) sheet of Na polyhedra is obtained (Fig. 2). The tetrahedra lie on both sides of this sheet and are connected to the octahedra by sharing O(3) and through the hydrogen bonds donated by W(1) (y direction), W(2) and W(3) (z direction). Two pairs of centrosymmetric W(4) and  $\text{NH}_4^+$  gather in groups where the four  $W \cdots N$  hydrogen bonds are the sides of a 'square' with corners N(1'), W(4)<sup>V</sup>, N(1) and W(4')<sup>II</sup>; the other eight hydrogen bonds of each group point to anionic oxygen atoms of the two contiguous layers (four each side). Since both a W(4) molecule and an  $\text{NH}_4^+$  ion belonging to differ-

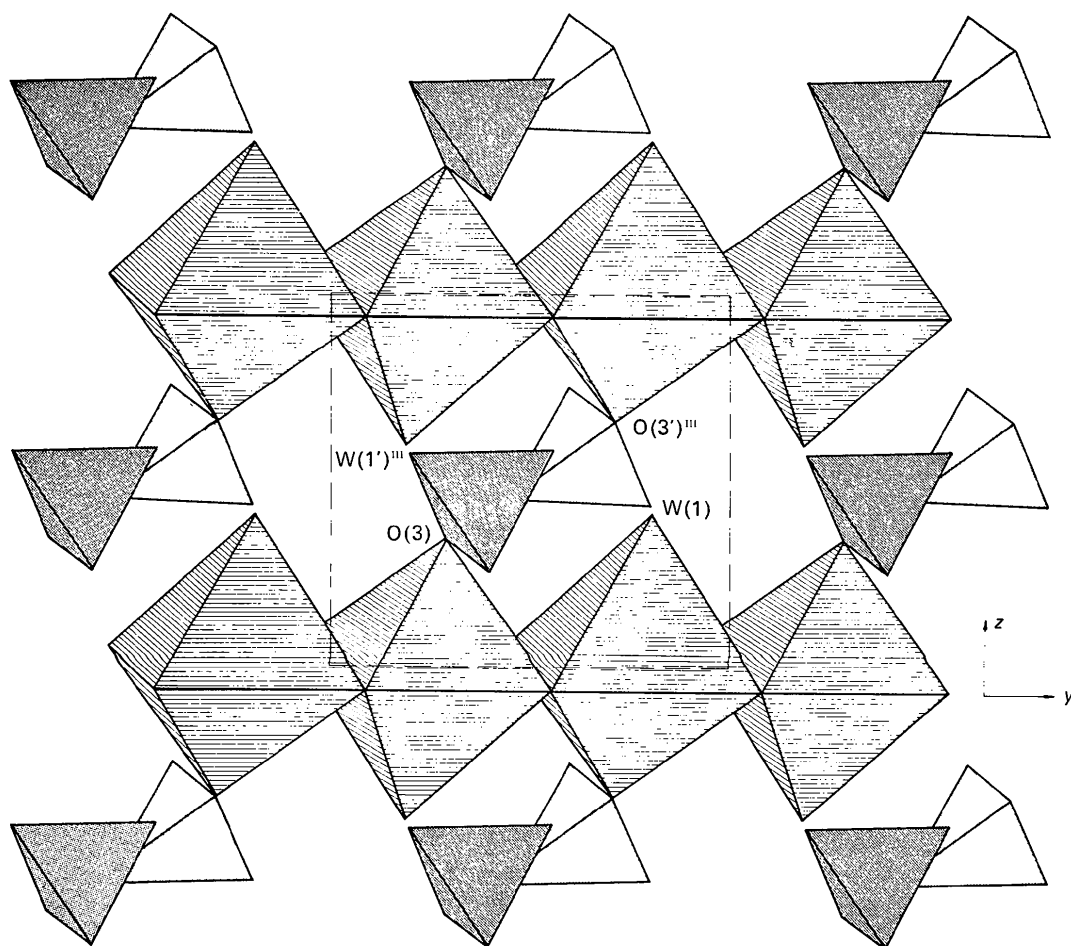


Fig. 2. Layer of Na octahedra and P tetrahedra in projection onto the (100) plane.

ent groups are donors of a hydrogen bond to O(1), infinite chains of 'squares' are formed along  $y$  (Fig. 1).

On the basis of the hydrogen-bond distribution an easy  $\{100\}$ , and perhaps  $\{001\}$ , cleavage seems possible; Groth (1921) reports an indistinct cleavage without crystallographic indications.

#### The twinning

Transformation ( $\frac{1}{2}100/\frac{1}{2}10/001$ ) of the coordinates given in Table 1 shows how marked is the  $C2/m$  pseudo-symmetry. In the pseudo-monoclinic cell the asymmetric unit is half a formula unit with P, Na, O(1), O(3) and  $W(1)$  on the 'mirror' plane which, in turn, relates the members of the pairs O(2) and O(4),  $W(2)$  and  $W(3)$ ,  $W(4)$  and N. The symmetry operations of  $C2/m$  fail geometrically by less than 0.01 Å with the exception of 0.05 Å for the  $W(4)$  and N pair; the difference between the lengths of 'equivalent' bonds is never larger than 0.02 Å. Of course, the crystallochemical difference between  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$  prevents stercorite from having higher symmetry; nevertheless, the tendency of water and ammonium to surround themselves with similar tetrahedral environments (Ferraris & Franchini-Angela, 1972; Khan & Baur, 1972) promotes the twinning. A local twofold or mirror symmetry could easily be established, on the twinning boundaries, by exchange of  $W(4)$  with  $\text{NH}_4^+$  within one of two contiguous 'squares' (Fig. 1).

$W(4)$  and ammonium apart, the pseudo-symmetry seems to be obeyed also by all the hydrogen atoms; in particular, the acidic hydrogen atom lies on the 'mirror' plane and the two hydrogen atoms of  $W(1)$  are related by the approximate  $m$  operation.

#### Accuracy of the structure

The intensities that receive contributions from the whole twin are undoubtedly approximations to the corresponding intensities scattered by a single crystal. The contribution to a reflexion from differently oriented individuals of the twin may be thought to be equivalent to that from a single crystal where the atoms can be displaced by a few hundredths of an Å from their average positions (see above); the final result will be an increase of the thermal motion. Such an effect is, however, quite small since the values of the root-mean displacements along the principal directions of the thermal motion (Table 6) are comparable with those of analogous structures. The largest vibration of all the atoms occurs roughly perpendicularly to  $y$  (Table 6), *i.e.* to the chains which characterize the structure; this seems reasonable.

All the bond angles and distances are normal and the e.s.d.'s, which, as expected, are slightly larger than those obtained for similar structures studied in this laboratory, should correctly describe the accuracy of the structure, at least for the positional parameters.

The research was supported by the Consiglio Nazionale delle Ricerche, Roma. We thank Professors I. D.

Table 6. Parameters characterizing the principal directions 1, 2, 3 of the thermal vibration: root-mean-square displacements ( $A$ ) and angles which the principal directions make with the crystallographic  $x$  ( $B$ ),  $y$  ( $C$ ) and  $z$  ( $D$ ) axes

		$A$ (Å)	$B$ (°)	$C$ (°)	$D$ (°)
P	1	0.133	127	18	86
	2	0.177	66	84	37
	3	0.115	46	74	127
Na	1	0.164	27	120	120
	2	0.213	64	87	37
	3	0.148	83	30	109
O(1)	1	0.17	119	10	91
	2	0.20	69	84	34
	3	0.12	38	82	124
O(2)	1	0.17	34	82	119
	2	0.21	67	96	31
	3	0.14	114	10	81
O(3)	1	0.20	120	26	110
	2	0.21	86	65	33
	3	0.15	30	84	115
O(4)	1	0.18	17	111	114
	2	0.21	74	75	35
	3	0.14	94	26	114
$W(1)$	1	0.17	24	123	115
	2	0.22	69	87	32
	3	0.15	79	33	109
$W(2)$	1	0.18	101	30	121
	2	0.23	59	72	55
	3	0.16	33	113	129
$W(3)$	1	0.19	121	39	53
	2	0.23	43	105	55
	3	0.15	63	55	124
$W(4)$	1	0.21	27	123	76
	2	0.25	103	62	29
	3	0.18	67	47	115
N	1	0.19	66	44	95
	2	0.22	79	99	19
	3	0.15	27	132	108

Brown, G. V. Gibbs and P. H. Ribbe for sending pre-prints of their papers and for their stimulating discussions with one of us (G.F.).

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## Structure Cristalline de l'Ester Méthylique du *N*-Acétyl L-tryptophane

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(Reçu le 3 septembre 1973, accepté le 19 octobre 1973)

*N*-Acetyl-L-tryptophan methyl ester crystallizes in the space group  $P2_12_12_1$  with cell dimensions  $a = 14.122$ ,  $b = 11.226$ ,  $c = 8.526$  Å and  $Z = 4$ . The structure was solved by the symbolic addition procedure; the final  $R$  index is 0.041. There is one intermolecular hydrogen bond  $\text{NH} \cdots \text{O} = \text{C}$  of 2.86 Å; molecular packing in the crystal is established by van der Waals forces between the two hydrophobic methyl groups and the aromatic ring. The conformation of the tryptophanyl residue, is defined by the dihedral angles:  $\varphi = -65.6^\circ$ ,  $\psi = 157.3^\circ$ ,  $\chi_1 = 172.6^\circ$  and  $\chi_2 = 87.8^\circ$  is very close to that of L-tryptophan formate. A short comparison between crystallographic results and energy calculations (semi-empirical and molecular orbital methods) is presented.

La structure cristalline de l'ester méthylique du *N*-acétyl L-tryptophane, en abrégé A Trp Me, de formule brute  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$ , a été établie dans le cadre d'une étude d'oligopeptides ayant un résidu aromatique. En ce qui concerne la phénylalanine et la tyrosine par exemple, l'étude cristallographique montre que la chaîne latérale de ces résidus ne peut adopter qu'un petit nombre de conformations bien définies (Cotrait, 1973).

### Partie expérimentale

#### Mesures

Des cristaux d'A Trp Me ont été obtenus par évaporation de solutions dans l'éthanol. Ils appartiennent au groupe spatial  $P2_12_12_1$  avec 4 molécules dans la maille dont les paramètres sont les suivants:

$$\begin{aligned} a &= 14,122 (\pm 0,004), \quad b = 11,226 (\pm 0,004), \\ c &= 8,526 (\pm 0,005) \text{ \AA} \\ V &= 1352 \text{ \AA}^3, \quad d = 1,277, \quad Z = 4. \end{aligned}$$

Environ 1450 réflexions indépendantes ont été collectées grâce à un diffractomètre automatique à 4 cercles Siemens pour la radiation  $K\alpha$  du cuivre ( $\lambda = 1,54178$  Å) et un angle de Bragg  $\theta$  limité à  $65^\circ$ . Aucune correction d'absorption n'a été faite, compte tenu des dimensions du cristal (cube de 0,2 mm de côté). Le coefficient moyen d'agitation thermique  $B_M$  évalué par la méthode de Wilson est égal à  $4,0 \text{ \AA}^2$ .

#### Détermination de la structure et affinement

La structure a été déterminée par la méthode d'addition symbolique (Karle & Karle, 1963): les réflexions 310 ( $E = 1,97$ ), 032 ( $E = 3,04$ ) et 109 ( $E = 2,39$ ) ont été choisies pour définir l'origine; les valeurs symboliques  $a$ ,  $b$  et  $c$  ont été respectivement attribuées aux réflexions 243 ( $E = 2,86$ ), 429 ( $E = 2,92$ ) et 555 ( $E = 2,59$ ). Les phases d'environ 210 réflexions ayant un facteur normalisé  $E$  supérieur à 1,30 ont pu être générées à partir des phases des 6 réflexions initiales, puis affinées par la formule de la tangente. Les sections de Fourier correspondantes révèlent pratiquement l'ensemble de la molécule.

L'affinement des coordonnées atomiques par méthode des moindres carrés avec des coefficients d'agitation thermique anisotropes  $\beta_{ij}$  pour les atomes de carbone, azote et oxygène et un coefficient d'agitation thermique isotrope moyen  $B_M = 4,0 \text{ \AA}^2$  pour les atomes d'hydrogène, conduit à un facteur  $R$  final de 0,041.\* Les paramètres atomiques sont rassemblés dans le Tableau 1. Les projections partielles de la structure parallèlement aux axes  $Oz$  et  $Oy$  respectivement sont représentées sur les Figs. 1(a) et 1(b).

\* La liste des facteurs de structure a été déposée au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 30254, 8 pp.). Des copies peuvent être obtenues en s'adressant à: The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, Angleterre.