

Hydrogen Bonding in the Crystalline State. Structure of $\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}$ (Hannayite), and Crystal-Chemical Relationships with Schertelite and Struvite

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Hannayite, $\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}$, crystallizes in space group $P\bar{1}$; $a=10.728$ (4), $b=7.670$ (3), $c=6.702$ (3) Å, $\alpha=97.87$ (8), $\beta=96.97$ (8), $\gamma=104.74$ (8)°, $Z=1$. The structure was solved by direct methods with 1725 observed reflexions measured on an automatic single-crystal diffractometer. All the H atoms, including those of NH_4^+ , were located from difference maps, and the anisotropic least-squares refinement led to $R=0.027$. The structure is built up of $(1\bar{1}0)$ layers of P and Mg coordination polyhedra sharing vertices. Layers are linked by hydrogen bonds of H_2O molecules and NH_4^+ ions, and are formed by two crossing systems of $[001]$ double chains and $[1\bar{1}\bar{1}]$ single chains of polyhedra. The three $\{101\}$, $\{1\bar{1}0\}$ and $\{100\}$ cleavages are related to structural features. A distorted coordination is shown by the $W(1)$ water molecule. The NH_4^+ ion has a CN of six, with four ordered hydrogen bonds tetrahedrally arranged and two electrostatic bonds; the latter are discussed on the basis of bond strength/bond length correlations. Structural similarities of hannayite, schertelite and struvite are analysed, and reactions occurring in natural guano material are discussed with crystal-chemical considerations.

Introduction

Hannayite was discovered and described by vom Rath (1879); it is found in guano deposits associated with newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$), struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$), schertelite [$\text{Mg}(\text{NH}_4)_2(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$] and bobierrite [$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] (Palache, Berman & Frondel, 1951). All these minerals are generated by reaction of the ammonium phosphate of guano with the magnesium of the surrounding basaltic rocks.

$\text{Mg}_3(\text{NH}_4)_2(\text{HPO}_4)_4 \cdot 8\text{H}_2\text{O}$ was also detected in human calculi with most of the above crystal phases (Gibson, 1974). The structures of newberyite (Sutor, 1967), struvite (Whitaker & Jeffery, 1970) and schertelite (Khan & Baur, 1972) have been determined; another related compound, $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, is isostructural with $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ whose structure is known (Tranqui, Durif, Guitel & Averbuch-Pouchot, 1968). A structural study of hannayite seemed necessary for a discussion of the crystal-chemical properties of the series of magnesium-ammonium orthophosphates, particularly to interpret the mechanisms of chemical reactions transforming them into one another.

The study of hannayite is part of a research programme on hydrogen bonding in the crystalline state (Catti & Ferraris, 1976). Hannayite and related compounds appear to be interesting in this respect, since they contain acidic hydrogen bonds and hydrogen bonds donated by H_2O molecules and NH_4^+ ions, all in the same structure. In particular, many problems are still unresolved about NH_4^+ and its bonding (Khan & Baur, 1972).

Experimental

Preparation, crystal data and morphology

A sample of synthetic hannayite was precipitated by mixing aqueous solutions of magnesium acetate, $\text{NH}_4\text{H}_2\text{PO}_4$ and ammonium acetate at room temperature (Frazier, Lehr & Smith, 1963). Small, colourless, tabular $\{1\bar{1}0\}$ crystals were obtained; most were aggregates of two or more individuals (iso-oriented along $[001]$). The single crystal selected for the measurements (elongated along $[001]$) was characterized by the three pinacoids $\{1\bar{1}0\}$ (prominent), $\{100\}$ and $\{101\}$; its dimensions were $0.19 \times 0.09 \times 0.05$ mm.

By least-squares refinement of 25θ values, measured by single-crystal diffractometry (Mo $K\alpha$ radiation), the following cell parameters were obtained: $a=10.728$ (4), $b=7.670$ (3), $c=6.702$ (3) Å, $\alpha=97.87$ (8), $\beta=96.97$ (8), $\gamma=104.74$ (8)°. By applying the transformation $010/\bar{1}\bar{1}0/001$ to the present reduced cell, the cell reported by Frazier *et al.* (1963) is obtained. Other physical data: $Z=1$, $V=521.23$ Å³; M.W. 637.054; $D_m=2.03$ (Frazier *et al.*, 1963), $D_c=2.030$ g cm⁻³; $F(000)=330$; $\mu(\text{Mo } K\alpha \text{ radiation})=5.8$ cm⁻¹.

The morphological cell determined by vom Rath (1879) and reported by Palache *et al.* (1951) ($\alpha=122.50$, $\beta=126.75$, $\gamma=54.15^\circ$, $a:b:c=0.699:1:0.974$) is obtained by the transformation $10\bar{1}/12\bar{1}/003$. The forms observed by vom Rath are transformed as follows: $\{100\} \rightarrow \{2\bar{1}0\}$, $\{110\} \rightarrow \{100\}$, $\{1\bar{1}0\} \rightarrow \{1\bar{1}0\}$, $\{001\} \rightarrow \{101\}$, $\{1\bar{1}3\} \rightarrow \{0\bar{1}1\}$.

Intensity measurements

A Philips PW 1100 four-circle single-crystal diffractometer was used for the collection of intensities. Meas-

urement conditions: $\lambda(\text{Mo } K\alpha)=0.71069 \text{ \AA}$ with a graphite monochromator, $\theta \leq 28^\circ$, $\theta-2\theta$ scan, $\Delta\theta=1.4^\circ$, scanning speed $0.035^\circ \text{ s}^{-1}$; each scan was performed up to three times if the preset intensity of 1000 counts s^{-1} had not been reached; background time=(scan time/2) $(I_{\text{bkg}}/I_{\text{peak}})^{1/2}$, attenuating filter inserted for peak intensities higher than 100 000 counts s^{-1} . Three standard reflexions (32 $\bar{1}$, 302 and 040) were periodically checked. A final set of 1725 independent observed reflexions was obtained [$I_o \geq 2\sigma(I_o)$].

Solution and refinement of the structure

MULTAN (Germain, Main & Woolfson, 1971) was used. Statistical tests on the distribution of intensities showed the presence of the symmetry centre; a solution of the structure was then obtained in the space group $P\bar{1}$, revealing all the P and Mg and some of the O atoms, with one of the three Mg atoms on the inversion centre. The positions of the remaining O atoms were given by subsequent Fourier synthesis. The least-squares isotropic refinement led to $R=0.054$; R was lowered to 0.044 by an anisotropic cycle, and a difference map revealed all the H atoms bonded to O and H(11) and H(12) of the NH_4^+ ion. After a cycle with the H atoms kept fixed ($R=0.033$), the following weighting scheme was introduced: $w=1/(0.0018|F_o|^2+1)$, with $|F_o|$ on 1.327 times the absolute scale and $0.11 \leq w \leq 0.93$. The two missing H atoms then appeared on a difference map, and a final refinement performed by varying non-hydrogen and H parameters separately led to $R=0.027$ and $R_w=0.036$.* Linear interpolations of Dirac-Slater atomic scattering factor tables (Cromer & Waber, 1965) and the least-squares program of Busing, Martin & Levy (1962) (in a slightly

modified version) were used for the refinement. No absorption or secondary extinction corrections were applied.

The final fractional coordinates and coefficients of the expression

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

for heavy atoms are listed in Table 1; fractional coordinates and isotropic thermal parameters of H atoms are shown in Table 2. The r.m.s. displacements along principal directions and the orientations of thermal ellipsoids for heavy atoms are given in Table 3.

Table 2. Fractional coordinates and isotropic vibrational parameters (\AA^2) of hydrogen atoms, with significant figures of the e.s.d.'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> |
|-------|-----------|------------|-----------|----------|
| H(1) | 0.248 (4) | 0.587 (5) | 0.840 (6) | 1.0 (7) |
| H(2) | 0.705 (4) | 0.779 (5) | 1.005 (6) | 0.9 (8) |
| H(3) | 0.027 (4) | -0.228 (5) | 0.644 (6) | 0.7 (7) |
| H(4) | 0.091 (4) | -0.258 (6) | 0.816 (7) | 2.2 (9) |
| H(5) | 0.225 (4) | 0.053 (5) | 1.267 (6) | 0.9 (8) |
| H(6) | 0.119 (3) | -0.104 (4) | 1.286 (5) | 0.2 (6) |
| H(7) | 0.231 (3) | -0.049 (5) | 0.676 (5) | 0.7 (7) |
| H(8) | 0.339 (4) | -0.107 (5) | 0.686 (5) | 0.6 (7) |
| H(9) | 0.589 (3) | 0.182 (5) | 0.876 (5) | 0.4 (7) |
| H(10) | 0.579 (3) | 0.057 (4) | 0.710 (5) | 0.2 (6) |
| H(11) | 0.147 (5) | 0.569 (6) | 0.340 (7) | 1.4 (9) |
| H(12) | 0.226 (4) | 0.462 (5) | 0.417 (6) | 0.8 (8) |
| H(13) | 0.182 (3) | 0.447 (5) | 0.194 (5) | 0.6 (7) |
| H(14) | 0.278 (4) | 0.620 (6) | 0.313 (7) | 2.4 (9) |

Discussion

Features of the structure and hydrogen bonding

Hannayite is made up of (1 $\bar{1}0$) layers formed by P and Mg coordination polyhedra (Fig. 1); NH_4^+ ions lie on both sides of each layer. The linking between layers is provided by hydrogen bonding only, and four independent hydrogen bonds out of fourteen are involved: three are donated by water molecules

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31835 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates and anisotropic vibrational parameters (\AA^2) of heavy atoms, with significant figures of the e.s.d.'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> ₁₁ | <i>B</i> ₂₂ | <i>B</i> ₃₃ | <i>B</i> ₁₂ | <i>B</i> ₁₃ | <i>B</i> ₂₃ |
|-------|-------------|-------------|-------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| P(1) | 0.12828 (6) | 0.33408 (8) | 0.75136 (2) | 0.61 (2) | 0.88 (2) | 0.74 (2) | 0.20 (2) | 0.15 (2) | 0.28 (2) |
| P(2) | 0.52884 (6) | 0.69239 (8) | 0.79383 (9) | 0.66 (2) | 0.66 (2) | 0.56 (2) | 0.12 (2) | 0.17 (2) | 0.17 (2) |
| Mg(1) | 0 | 0 | 1 | 0.85 (4) | 1.15 (4) | 0.88 (4) | 0.12 (3) | 0.18 (3) | 0.39 (3) |
| Mg(2) | 0.40280 (8) | 0.2405 (1) | 0.6622 (1) | 0.86 (3) | 0.87 (3) | 0.76 (3) | 0.18 (2) | 0.21 (2) | 0.18 (2) |
| N | 0.2094 (2) | 0.5266 (4) | 0.3144 (4) | 1.69 (9) | 2.37 (9) | 1.60 (9) | 0.80 (8) | 0.56 (7) | 0.53 (7) |
| O(1) | -0.0067 (2) | 0.2961 (3) | 0.6275 (3) | 0.99 (6) | 2.00 (8) | 1.28 (7) | 0.45 (6) | 0.46 (5) | 0.50 (5) |
| O(2) | 0.1272 (2) | 0.2282 (2) | 0.9299 (3) | 1.02 (6) | 1.60 (7) | 1.27 (7) | 0.17 (5) | 0.15 (5) | 0.64 (5) |
| O(3) | 0.2292 (2) | 0.3025 (3) | 0.6206 (3) | 1.23 (6) | 1.77 (7) | 1.14 (7) | 0.60 (6) | 0.46 (5) | 0.47 (5) |
| O(4) | 0.1723 (2) | 0.5455 (3) | 0.8522 (3) | 1.34 (7) | 1.14 (6) | 2.12 (8) | 0.20 (5) | 0.53 (6) | 0.12 (5) |
| O(5) | 0.6233 (2) | 0.7702 (2) | 1.0107 (3) | 0.97 (6) | 1.84 (7) | 0.82 (6) | 0.28 (5) | 0.25 (5) | 0.23 (5) |
| O(6) | 0.5928 (2) | 0.8057 (2) | 0.6441 (3) | 1.42 (7) | 1.07 (6) | 0.97 (6) | 0.14 (5) | 0.48 (5) | 0.35 (5) |
| O(7) | 0.5184 (2) | 0.4926 (2) | 0.7377 (3) | 1.44 (7) | 1.02 (7) | 1.57 (7) | 0.23 (5) | 0.34 (5) | 0.30 (5) |
| O(8) | 0.4021 (2) | 0.7363 (2) | 0.8348 (3) | 0.98 (6) | 1.49 (7) | 1.43 (7) | 0.38 (5) | 0.39 (5) | 0.37 (5) |
| W(1) | 0.0550 (2) | -0.1770 (3) | 0.7761 (3) | 2.18 (8) | 1.88 (8) | 1.32 (7) | 0.89 (6) | 0.39 (6) | 0.14 (6) |
| W(2) | 0.1476 (2) | -0.0290 (3) | 1.2031 (3) | 1.27 (7) | 2.27 (8) | 1.74 (8) | -0.01 (6) | -0.26 (5) | 1.04 (6) |
| W(3) | 0.2991 (2) | -0.0389 (2) | 0.6255 (3) | 1.30 (7) | 1.31 (7) | 1.55 (7) | 0.22 (5) | 0.29 (5) | 0.50 (5) |
| W(4) | 0.5737 (2) | 0.1605 (2) | 0.7495 (3) | 1.50 (7) | 1.18 (7) | 1.20 (7) | 0.51 (5) | 0.23 (5) | 0.15 (5) |

$[W(1) \cdots O(4_2), W(3) \cdots O(8_2), W(4) \cdots O(6_2)]^*$ and one is donated by the ion $[N \cdots O(1_8')]$.

* Symbols with a prime denote atoms subjected to the transformation $\bar{x}, \bar{y}, \bar{z}$; subscripts denote the following translations: (1) $+a, +b, +2c$; (2) $-b$; (3) $+a, +b, +c$; (4) $+2c$; (5) $+a$; (6) $-c$; (7) $+c$; (8) $+b, +c$.

Each layer can be described as a two-dimensional network of P tetrahedra and Mg octahedra sharing vertices (Fig. 2); this network is built up by a system of [001] double chains and a system of [11 $\bar{1}$] single chains of polyhedra, which cross each other at a 128.8° angle. Each double chain is formed by two centrosym-

Table 3. Parameters characterizing the principal directions of thermal vibration for P, Mg, N and O atoms: *r.m.s. displacements (A) and angles which the principal directions make with x (B), y (C) and z (D)*

| | A | B | C | D | | A | B | C | D |
|-------|---------|-----|------|-----|------|---------|-----|-----|-----|
| P(1) | 0.090 Å | 57° | 123° | 44° | O(5) | 0.113 Å | 33° | 91° | 68° |
| | 0.110 | 100 | 36 | 63 | | 0.156 | 105 | 3 | 95 |
| | 0.086 | 35 | 78 | 122 | | 0.097 | 119 | 93 | 22 |
| P(2) | 0.091 | 65 | 62 | 59 | O(6) | 0.122 | 92 | 42 | 60 |
| | 0.097 | 143 | 38 | 92 | | 0.144 | 24 | 118 | 75 |
| | 0.077 | 115 | 114 | 31 | | 0.090 | 114 | 119 | 34 |
| Mg(1) | 0.106 | 42 | 95 | 58 | O(7) | 0.135 | 34 | 113 | 126 |
| | 0.130 | 118 | 29 | 71 | | 0.144 | 58 | 100 | 40 |
| | 0.091 | 118 | 119 | 39 | | 0.111 | 80 | 25 | 105 |
| Mg(2) | 0.104 | 67 | 58 | 62 | O(8) | 0.131 | 108 | 43 | 137 |
| | 0.110 | 141 | 38 | 99 | | 0.141 | 86 | 48 | 57 |
| | 0.093 | 119 | 108 | 29 | | 0.105 | 18 | 95 | 113 |
| N | 0.146 | 50 | 122 | 50 | W(1) | 0.146 | 124 | 37 | 121 |
| | 0.175 | 79 | 33 | 81 | | 0.172 | 42 | 63 | 97 |
| | 0.127 | 138 | 84 | 41 | | 0.123 | 113 | 67 | 32 |
| O(1) | 0.128 | 122 | 105 | 30 | W(2) | 0.127 | 54 | 54 | 118 |
| | 0.161 | 99 | 23 | 77 | | 0.203 | 123 | 43 | 59 |
| | 0.105 | 33 | 107 | 64 | | 0.110 | 53 | 110 | 44 |
| O(2) | 0.115 | 34 | 100 | 64 | W(3) | 0.134 | 32 | 114 | 66 |
| | 0.157 | 114 | 36 | 62 | | 0.147 | 110 | 55 | 43 |
| | 0.107 | 113 | 124 | 40 | | 0.114 | 66 | 45 | 123 |
| O(3) | 0.124 | 45 | 125 | 57 | W(4) | 0.125 | 79 | 118 | 24 |
| | 0.152 | 79 | 35 | 77 | | 0.139 | 30 | 75 | 98 |
| | 0.104 | 133 | 90 | 36 | | 0.115 | 118 | 32 | 68 |
| O(4) | 0.129 | 32 | 125 | 114 | | | | | |
| | 0.170 | 72 | 109 | 25 | | | | | |
| | 0.118 | 64 | 42 | 96 | | | | | |

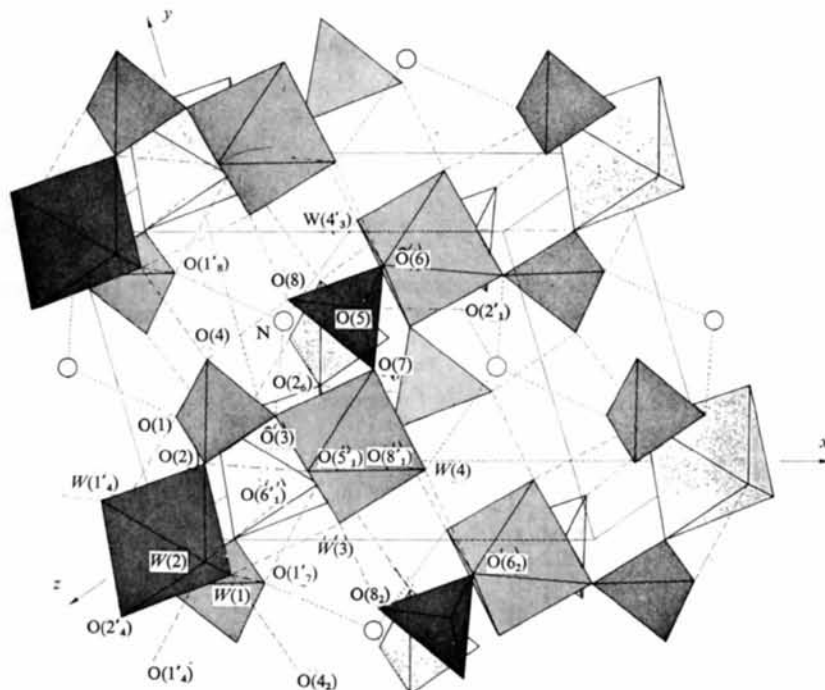


Fig. 1. Orthographic projection down z of the unit cell of $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$ (hannayite). Dashed-dotted, dashed and dotted lines show acidic, water and ammonium hydrogen bonds respectively.

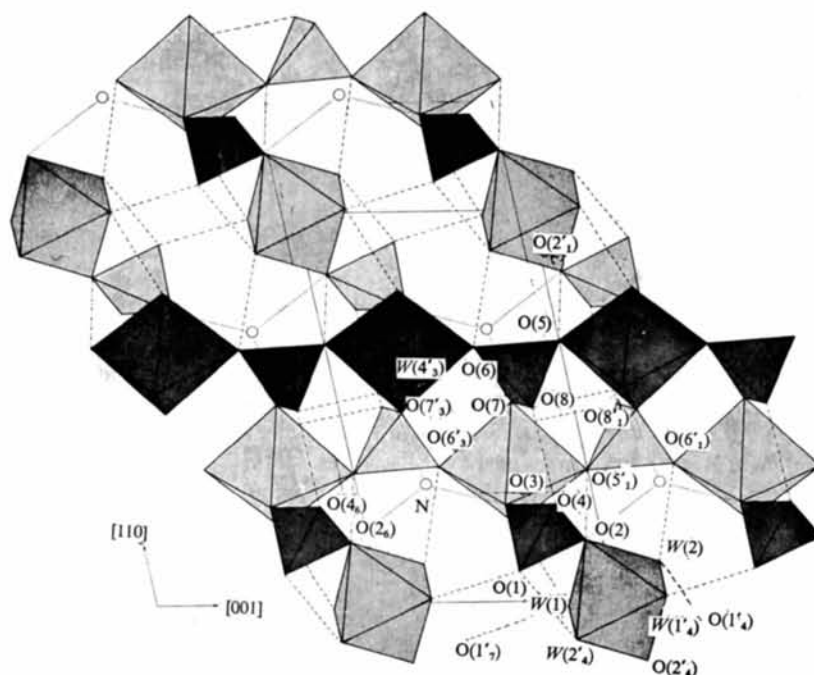


Fig. 2. Projection of the unit cell of $Mg_3(NH_4)_2(HPO_4)_4 \cdot 8H_2O$ (hannayite) onto the $(1\bar{1}0)$ plane. The light cell contour refers to the upper parallel plane. Hydrogen bonds are drawn as in Fig. 1.

metric chains of alternating P tetrahedra and Mg octahedra. Holes elongated along $[11\bar{1}]$, delimited by the two systems of chains, appear in the layer; holes of adjacent layers build up $[010]$ empty channels throughout the structure.

Cyclic systems of four P tetrahedra linked by acidic hydrogen bonds can be observed inside the layers; these rings are planar and centrosymmetric with respect to centres in positions of the type $\frac{1}{2}, \frac{1}{2}, 0$. The $[11\bar{1}]$ chains within each layer are linked to each other by two hydrogen bonds donated by water molecules $[W(1) \cdots O(1')]$ and $[W(2) \cdots O(6'_1)]$ and two donated by the NH_4^+ ion $[N \cdots O(3)]$ and $[N \cdots O(2_6)]$; such bonds bridge the holes between the chains. The remaining four hydrogen bonds [donated by $W(2)$, $W(3)$, $W(4)$ and N] tie coordination polyhedra inside the chains. $\{101\}$, $\{1\bar{1}0\}$ and $\{100\}$ cleavages were observed by vom Rath (1879). The $\{1\bar{1}0\}$ cleavage is easily understandable, since it is parallel to the layers and involves the breaking of hydrogen bonds only; instead, each of the $\{101\}$ and $\{100\}$ cleavages cuts one system of chains and is parallel to the other. Since the relative importance of these cleavages was not unambiguously stated by vom Rath, the bonding between layers would not seem to be very weak, as compared to bonding of coordination polyhedra within the chains; actually, the splitting of parallel layers causes the coordination sphere of NH_4^+ to break off, and this process could require a fairly substantial energy.

Coordination and hydrogen bonds of O atoms

The geometrical features of hydrogen bridges between O atoms are shown in Table 4. The two acidic

bonds (2.553 and 2.655 Å) should have comparatively medium and low strengths, respectively, with reference to typical distances for this kind of bond. Contacts of water molecules range from 2.677 to 2.919 Å, with prevalence of medium-strong hydrogen bonds. Distances and angles involving H atoms are quite satisfactory, taking into account the well known effect of 'shortening' of the O-H distance when X-ray diffraction data are used.

Table 4. *Interatomic distances, uncorrected and corrected (C) for thermal motion (riding model), and O-P-O angles for the two independent PO_4 groups*

The e.s.d.'s are 0.002 and 0.003 Å for P-O and O-O distances, respectively, and 0.1° for the angles.

| | | C | | C | |
|-----------|---------|---------|-----------|---------|---------|
| P(1)-O(1) | 1.517 Å | 1.524 Å | P(2)-O(5) | 1.611 Å | 1.617 Å |
| P(1)-O(2) | 1.535 | 1.541 | P(2)-O(6) | 1.529 | 1.535 |
| P(1)-O(3) | 1.519 | 1.525 | P(2)-O(7) | 1.499 | 1.507 |
| P(1)-O(4) | 1.595 | 1.604 | P(2)-O(8) | 1.528 | 1.535 |
| Average | 1.542 | 1.549 | Average | 1.542 | 1.549 |
| O(1)-O(2) | 2.532 Å | 112.1° | O(5)-O(6) | 2.501 Å | 105.6° |
| O(1)-O(3) | 2.526 | 112.7 | O(5)-O(7) | 2.523 | 108.4 |
| O(1)-O(4) | 2.501 | 107.0 | O(5)-O(8) | 2.452 | 102.7 |
| O(2)-O(3) | 2.525 | 111.6 | O(6)-O(7) | 2.522 | 112.8 |
| O(2)-O(4) | 2.498 | 105.9 | O(6)-O(8) | 2.526 | 111.3 |
| O(3)-O(4) | 2.505 | 107.1 | O(7)-O(8) | 2.554 | 115.1 |
| Average | 2.515 | 109.4 | Average | 2.513 | 109.3 |

The configurations of water molecules and their environments are well defined, and can be classified (Ferraris & Franchini-Angela, 1972) as follows: $W(2)$ belongs to class 1, type D ($\epsilon_1 = 25^\circ$); $W(3)$ to class 1', type J ($\epsilon_1 = 51^\circ$); and $W(1)$ and $W(4)$ to class 2, type

H. The bond directions $W(1)-Mg(1)$ and $W(1)-H(7)$ are strongly shifted from the two lone-pair orbital directions of $W(1)$: their angles with the plane of the water molecule are $\epsilon_2=18$ and $\epsilon_3=85^\circ$ respectively. In the survey of crystalline hydrates quoted above, the lowest angle reported is 23° , with a smaller distortion than that shown here by $W(1)$. Such a highly distorted environment is actually very close to a trigonal planar sp^2 coordination (as in class 1), with the fourth cation interacting electrostatically along a direction roughly perpendicular to the plane. A more regular situation can be observed for $W(4)$.

Tetrahedral and trigonal coordinations, respectively, are shown by O(1), O(2), O(6), O(8) and by O(3), O(4), O(5), with distortions. O(7), which would seem to coordinate only P(2) and Mg(2) with an angle of 147° , is a peculiar case; as discussed below, however, this O should interact ionically with the NH_4^+ ion and thus assume a trigonal planar coordination: the angles of O(7)-N with the other two bond directions are 106 and 107° , respectively, and give a perfect planarity.

The ammonium ion

Some problems are still unresolved in the crystal chemistry of NH_4^+ ions; this is because of the limited number of structures where H atoms have been located accurately by neutron diffraction or even inaccurately by X-ray difference maps. A summary was given by Khan & Baur (1972). They pointed out that: (i) the number of contacts of the N atom varies from four to nine, whereas large alkaline cations always have a CN higher than five; (ii) when the CN of NH_4^+ is four, four regular hydrogen bonds are usually formed, with a roughly tetrahedral arrangement of the acceptors; (iii) when the CN of NH_4^+ is greater than four, then either the ion is disordered, or polyfurcated hydrogen bonds are present, or no hydrogen bonding is present.

Table 5. *Interatomic distances (Å) and O-Mg-O angles ($^\circ$) in the Mg coordination polyhedra*

The e.s.d.'s are 0.002 and 0.003 Å for Mg-O and O-O distances, respectively, and 0.1° for the angles.

| | | | |
|----------------------------|------------------------------|---------------------------------------|-------|
| Mg(1)-O(2) | 2.077 | Mg(2)-O(3) | 2.033 |
| Mg(1)- $W(1)$ | 2.123 | Mg(2)-O(5 _i) | 2.254 |
| Mg(1)- $W(2)$ | 2.037 | Mg(2)-O(6 _j) | 2.043 |
| Mg(1)-O(2 _i) | 2.077 | Mg(2)-O(7) | 1.974 |
| Mg(1)- $W(1_4)$ | 2.123 | Mg(2)- $W(3)$ | 2.114 |
| Mg(1)- $W(2_4)$ | 2.037 | Mg(2)- $W(4)$ | 2.119 |
| Average | 2.079 | Average | 2.090 |
| O(2)- $W(1)$ | O(2 _i)- $W(1_4)$ | 3.004 | 91.3 |
| O(2)- $W(2)$ | O(2 _i)- $W(2_4)$ | 2.899 | 89.6 |
| O(2)- $W(1_4)$ | O(2 _i)- $W(1)$ | 2.935 | 88.7 |
| O(2)- $W(2_4)$ | O(2 _i)- $W(2)$ | 2.918 | 90.4 |
| $W(1)$ - $W(2)$ | $W(1_4)$ - $W(2_4)$ | 2.883 | 87.7 |
| $W(1)$ - $W(2_4)$ | $W(1_4)$ - $W(2)$ | 3.000 | 92.3 |
| Average | | 2.940 | 90.0 |
| O(3)-O(5 _i) | 2.966 | 87.4 | |
| O(3)-O(6 _j) | 2.951 | 92.8 | |
| O(3)-O(7) | 3.037 | 98.1 | |
| O(3)- $W(3)$ | 2.905 | 88.9 | |
| $W(3)$ -O(5 _i) | 2.854 | 81.5 | |
| O(5 _i)-O(7) | 3.036 | 91.6 | |
| O(7)-O(6 _j) | 3.078 | 100.0 | |
| O(6 _j)- $W(3)$ | 2.855 | 86.7 | |
| $W(4)$ - $W(3)$ | 2.912 | 86.9 | |
| $W(4)$ -O(5 _i) | 2.915 | 83.5 | |
| $W(4)$ -O(7) | 2.768 | 85.0 | |
| $W(4)$ -O(6) | 3.082 | 95.5 | |
| Average | 2.946 | 89.8 | |
| O(2)-O(2 _i) | 180.0 | O(5 _i)-O(6 _j) | 168.3 |
| $W(1)$ - $W(1_4)$ | 180.0 | $W(3)$ -O(7) | 169.9 |
| $W(2)$ - $W(2_4)$ | 180.0 | $W(4)$ -O(3) | 170.5 |

In hannayite four ordered hydrogen bonds have been revealed by locating all the H atoms of NH_4^+ (Table 5). The arrangement both of the acceptors and of the H atoms around N is satisfactorily tetrahedral. However, the CN of the NH_4^+ ion is not four but six, since

Table 6. *Interatomic distances (Å) and angles ($^\circ$) in hydrogen bonds not involving nitrogen atoms*

The e.s.d.'s are 0.003 Å and 0.1° , respectively, for distances and angles where hydrogen atoms are not present, and 0.04 Å and 4° where hydrogen atoms are involved.

| A | B | C | D | E | AC | AB | BC | ABC | CE | CD | DE | CDE | BCD | ACE | | |
|--------------------|------|------|----------|--------|--------------------|--------------------|-------|------|-------|------|-------|------|------|-----|-----|-------|
| | P(1) | O(4) | H(1) | ⋯⋯ | O(8) | | | | 2.553 | 0.81 | 1.77 | 164 | 108 | | | |
| | P(2) | O(5) | H(2) | ⋯⋯ | O(2 _i) | | | | 2.655 | 0.87 | 1.82 | 162 | 113 | | | |
| O(1 _j) | ⋯⋯ | H(3) | - $W(1)$ | -H(4) | ⋯⋯ | O(4 _j) | 2.677 | 1.79 | 0.90 | 167 | 2.808 | 0.86 | 1.96 | 169 | 100 | 92.7 |
| O(6 _j) | ⋯⋯ | H(5) | - $W(2)$ | -H(6) | ⋯⋯ | O(1 _i) | 2.853 | 1.95 | 0.92 | 166 | 2.692 | 0.88 | 1.86 | 157 | 109 | 127.0 |
| $W(1)$ | ⋯⋯ | H(7) | - $W(3)$ | -H(8) | ⋯⋯ | O(8 _j) | 2.919 | 2.13 | 0.83 | 159 | 2.724 | 0.87 | 1.87 | 172 | 104 | 88.2 |
| O(8 _j) | ⋯⋯ | H(9) | - $W(4)$ | -H(10) | ⋯⋯ | O(6 _j) | 2.752 | 1.94 | 0.83 | 167 | 2.782 | 0.82 | 1.97 | 174 | 109 | 112.0 |

Table 7. *Interatomic distances (Å) and angles ($^\circ$) in hydrogen bonds involving the ammonium ion*

The e.s.d.'s are 0.003 Å and 0.1° , respectively, for distances and angles where hydrogen atoms are not present, and 0.04 Å and 4° where hydrogen atoms are involved.

| A | B | C | AC | AB | BC | ABC | A | B | C | B' | A' | ACA' | BCB' | AA' | BB' | |
|---------|----|--------------------|-------|------|------|-----|--------------------|----|-------|----------|----|--------------------|-------|-----|-------|------|
| N-H(11) | ⋯⋯ | O(1 ₈) | 2.880 | 0.84 | 2.05 | 171 | O(1 ₈) | ⋯⋯ | H(11) | -N-H(12) | ⋯⋯ | O(3) | 109.7 | 108 | 4.703 | 1.43 |
| N-H(12) | ⋯⋯ | O(3) | 2.874 | 0.93 | 1.96 | 170 | O(1 ₈) | ⋯⋯ | H(11) | -N-H(13) | ⋯⋯ | O(2 ₆) | 111.1 | 107 | 4.914 | 1.41 |
| N-H(13) | ⋯⋯ | O(2 ₆) | 3.077 | 0.91 | 2.18 | 171 | O(1 ₈) | ⋯⋯ | H(11) | -N-H(14) | ⋯⋯ | $W(4_3)$ | 101.4 | 108 | 4.556 | 1.40 |
| N-H(14) | ⋯⋯ | $W(4_3)$ | 3.007 | 0.89 | 2.13 | 169 | O(3) | ⋯⋯ | H(12) | -N-H(13) | ⋯⋯ | O(2 ₆) | 99.6 | 109 | 4.548 | 1.49 |
| | | | | | | | O(3) | ⋯⋯ | H(12) | -N-H(14) | ⋯⋯ | $W(4_3)$ | 125.1 | 111 | 5.218 | 1.50 |
| | | | | | | | O(2 ₆) | ⋯⋯ | H(13) | -N-H(14) | ⋯⋯ | $W(4_3)$ | 109.9 | 114 | 4.981 | 1.51 |

two other contacts are present besides the hydrogen bridges: $N \cdots O(7_3)$ and $N \cdots O(4_6)$, 3.021 and 3.104 Å respectively; the next contact, $N-W(1_7)$ (3.298 Å), can be considered to be outside the coordination sphere of NH_4^+ . The NH_4^+ ion is then bonded to $O(7_3)$ and $O(4_6)$ by a purely electrostatic interaction, playing the same role of a large alkaline cation, such as Rb^+ or Cs^+ , in this respect. This double behaviour of NH_4^+ as an (ordered) hydrogen-bonding donor group and (at the same time) a strongly electropositive large cation is probably much more common in crystals than is believed; it is then likely that coordination numbers of NH_4^+ higher than four can often be explained without supposing disordered or polyfurcated bonds.

Coordination polyhedra and bond length/bond strength relationships

By considering the distances and angles reported in Tables 6 and 7, the P(2) and Mg(2) coordination polyhedra appear to be significantly more distorted than those surrounding P(1) and Mg(1). Actually, the former polyhedra belong to [001] double chains where they share three and four vertices, respectively, whereas the latter belong to [111] single chains and share only two vertices with neighbours. In particular, the three distortion indices (Baur, 1974) of P(1) and P(2) tetrahedra for the P–O and O–O distances and the O–P–O angles are 0.018, 0.005, 0.025 and 0.023, 0.010, 0.034 respectively; the average values for acidic orthophosphates reported by Baur are 0.017, 0.011 and 0.025. It may be inferred that not only sharing edges (Baur, 1974), but also sharing vertices, may increase the distortion of coordination polyhedra.

A calculation of bond-strength values in the structure was performed with the 'universal' third-row relationship $s = (R/1.622)^{-4.29}$ of Brown & Shannon (1973) for P–O and Mg–O bonds, and the s vs O \cdots O distance curve of Brown (1976) for hydrogen bonds; the

results are shown in Table 8. Computing the s values of N–H \cdots O bonds with the same curve as for O–H \cdots O bonds was clearly a rough approximation, owing to the lack of an appropriate curve: apparently, the bond strengths have been underestimated, except perhaps for the H(14) \cdots W(4) bond. The most interesting result is that the evident underbonding of O(7) and O(4) ($\sum s_i = 1.83$ and 1.90 v.u. respectively) is in full agreement with their being ionically coordinated to the NH_4^+ ion. The curve used for the bond strengths of O–H \cdots O bonds seems to work better here than in previous cases (Catti & Ferraris, 1976).

Structural properties and chemical reactions of hannayite, schertelite and struvite

All three structures show a common feature: they are formed by layers of PO_4 tetrahedra and Mg octahedra, with NH_4^+ ions sandwiched between them. Layers are (110) in hannayite, (010) in schertelite and (001) in struvite, with distances of 6.91, 5.91 and 5.60 Å respectively. The coordination polyhedra are more or less condensed (by sharing vertices) within the layers according to the different H_2O/Mg and Mg/P stoichiometric ratios: double and single infinite chains are present in hannayite, whereas schertelite contains isolated groups formed by a Mg octahedron sharing two *trans* vertices with two P tetrahedra, and in struvite all coordination polyhedra are isolated.

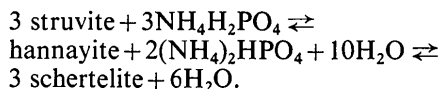
In the light of these crystal-chemical relationships, the transformation reactions of the three minerals in the presence of aqueous solutions can be discussed. As reported (Frazier *et al.*, 1963), several complex chemical alterations affecting the formation of mineral phases occur in guano deposits: aeration and nitrification, leaching and precipitation reactions. Some of these changes undergone by the natural material have been reproduced in laboratory studies concerning the behaviour of hannayite, schertelite and struvite in the

Table 8. *Electrostatic balance*

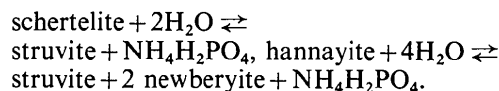
See text for explanation.

| | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) | O(7) | O(8) | W(1) | W(2) | W(3) | W(4) | $\sum s_i$ |
|------------|------|------|------|------|------|------|------|------|------|------|------|------|------------|
| P(1) | 1.33 | 1.27 | 1.33 | 1.08 | | | | | | | | | 5.01 |
| P(2) | | | | | 1.03 | 1.29 | 1.40 | 1.29 | | | | | 5.01 |
| Mg(1) | | 0.35 | | | | | | | 0.32 | 0.38 | | | 2.10 |
| Mg(2) | | | 0.38 | | 0.24 | 0.37 | 0.43 | | | | 0.32 | 0.32 | 2.06 |
| H(1) | | | | 0.66 | | | | 0.34 | | | | | 1.00 |
| H(2) | | 0.25 | | | 0.75 | | | | | | | | 1.00 |
| H(3) | 0.23 | | | | | | | | 0.77 | | | | 1.00 |
| H(4) | | | | 0.16 | | | | | 0.84 | | | | 1.00 |
| H(5) | | | | | | 0.13 | | | | 0.87 | | | 1.00 |
| H(6) | 0.22 | | | | | | | | | 0.78 | | | 1.00 |
| H(7) | | | | | | | | | 0.11 | | 0.89 | | 1.00 |
| H(8) | | | | | | | | 0.20 | | | 0.80 | | 1.00 |
| H(9) | | | | | | | | 0.19 | | | | 0.81 | 1.00 |
| H(10) | | | | | | 0.17 | | | | | | 0.83 | 1.00 |
| H(11) | 0.12 | | | | | | | | | | | | |
| H(12) | | | 0.12 | | | | | | | | | | |
| H(13) | | 0.05 | | | | | | | | | | | |
| H(14) | | | | | | | | | | | | 0.07 | |
| $\sum s_i$ | 1.90 | 1.92 | 1.83 | 1.90 | 2.02 | 1.96 | 1.83 | 2.02 | 2.04 | 2.03 | 2.01 | 2.03 | |

presence of aqueous ammonium phosphate solutions. Particularly, struvite is reported to react with a saturated solution of ammonium dihydrogen phosphate to form hannayite, which is then slowly replaced by schertelite; these reactions can be summarized as follows:



Inversely, schertelite and hannayite undergo hydrolytic reactions dissolving incongruently in water:



Such transformations also probably occur in human renal liquids under pathological conditions. They can be explained by the strong tendency of systems with this chemical composition to give crystals characterized by a layered structure, where the amount of NH_4^+ ions between layers and the degree of condensation of coordination polyhedra inside the layers vary according to the concentrations of the different chemical species. When hannayite transforms into schertelite, for instance, the condensation of polyhedra decreases strongly, with the formation of isolated

$\text{Mg}(\text{H}_2\text{O})_4(\text{OPO}_2\text{OH})_2$ groups. The first bonds which break in hannayite are likely to be $\text{Mg}(2)-\text{O}(3)$ and $\text{Mg}(2)-\text{O}(7)$ (Fig. 2), since they involve the most underbonded O atoms in the structure ($\sum s_i = 1.83$ v.u.); this should be true both for complete solubilization of crystals and for incomplete solubilization with partial solid-state reaction. The latter mechanism would agree with the fact that, by breaking $\text{Mg}(2)-\text{O}(3)$, isolated

groups of $\text{Mg}(\text{H}_2\text{O})_4(\text{OPO}_2\text{OH})_2$ are formed, which could build up the schertelite crystal framework.

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Crystallographic Studies of Bis-(*N-p*-tolylsalicylaldiminato)copper(II)

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The structure of bis-(*N-p*-tolylsalicylaldiminato)copper(II) has been determined by the photographic method and refined to $R=0.09$. The crystals are monoclinic needles, $a=13.584$, $b=7.546$, $c=12.221$ Å, $\beta=110.8^\circ$, $Z=2$. The structure consists of discrete molecules in which the metal atom exhibits *trans*-planar fourfold coordination and has Cu–O 1.899 and Cu–N 2.010 Å. The *p*-tolyl group is inclined by 124° to the salicylaldimine plane.

Introduction

In order to gather more information on the structural features and their dependence on various steric and

electronic effects in the presence of different types of substituents on the N of the salicylaldimine (designated hereafter sim) moiety, considerable attention has been given to the study of solid-state properties. Holm,