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Synthetic Struvite, $MgNH_4PO_4.6H_2O$: Correct Polarity and Surface Features of Some Complementary Forms

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Abstract

Struvite, $MgNH_4PO_4.6H_2O$, $M_r = 245{\cdot}4$, is orthorhombic, $Pmn2_1$. To establish the correct polarity, two refinements were completed from diffractometer Friedel-pair intensities measured with graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å) using two crystals grown under different, controlled, conditions: $a = 6{\cdot}955\,(1)$, $b = 6{\cdot}142\,(1)$, $c = 11{\cdot}218\,(2)$ Å (average cell parameters obtained and refined from 20 reflexions, $55° \leq 2\theta \leq 110°$), $V = 479{\cdot}2\,(1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}70$ Mg m^{-3}, $F(000) = 260$, μ(Cu $K\alpha$) $= 3{\cdot}64$ mm^{-1}, room temperature. Final R values for the correct and incorrect polarity were 0·0322, 0·0402 for the first crystal (764 reflexions, 723 Friedel pairs) and 0·0331, 0·0419 for the second crystal (863 reflexions, 805 Friedel pairs). These values, taken with the relative F_o, F_c values of the Friedel pairs and with the results from a test proposed by Rogers [*Acta Cryst.* (1981), A**37**, 734–741], establish the correct polarity, identical for both crystals, at a very high confidence level. In order to complete a more accurate, room-temperature, determination, a third crystal was employed for graphite-monochromatized Mo $K\alpha$ diffractometry ($\lambda = 0{\cdot}71069$ Å): $a = 6{\cdot}966\,(1)$, $b = 6{\cdot}142\,(1)$, $c = 11{\cdot}217\,(2)$ Å (parameters from 24 reflexions, $22° \leq 2\theta \leq 43°$), $V = 479{\cdot}9\,(1)$ Å^3, $D_x = 1{\cdot}70$ Mg m^{-3}, μ(Mo $K\alpha$) $= 0{\cdot}40$ mm^{-1}. Final $R = 0{\cdot}0286$ for 989 independent reflexions. Within the chosen experimental conditions, the ammonium ion does not appear to be disordered contrary to the results from former investigations of struvite and the isomorphous arsenstruvite. The correct polarity has been correlated with crystal morphology and with surface features of some important complementary forms.

Introduction

One of the aims of the present X-ray investigation of struvite was to establish its correct polarity, as yet unknown, which is indispensable for the unambiguous correlation of morphology and structure and for the correct interpretation of the morphologic modifications observed for this phosphate as a function of the supersaturation and pH for the mother solutions. The knowledge of the polarity could therefore allow the interpretation of several experimental results (*e.g.* Abbona & Boistelle, 1979; Wevers, Kars & Schuiling, 1981). Besides, an accurate redetermination of the struvite structure might contribute to the understanding of the behaviour of the NH_4^+ ion. The more recent, and the only accurate, X-ray analysis of struvite, based on crystals of biological origin from a rather unusual source, supported the assumption of an ammonium ion rotating, possibly unevenly, around the N···O(1) direction, Fig. 2 [Whitaker & Jeffery, 1970*a*, *b*; WJ(*a*, *b*) hereinafter]. The situation around N in difference Fourier maps of the isomorphous arsenstruvite, $MgHN_4AsO_4.6H_2O$, appeared similar to that found for struvite, but it was interpreted in terms of fractional occupancies of two H atoms in general positions with their symmetry equivalents related by the mirror plane orthogonal to the x axis, giving altogether four atoms, including H(1), Fig. 2, around the special position occupied by N (Ferraris & Franchini-Angela, 1973).

Experimental

Crystal habit

The crystals for the present analysis were prepared by mixing, without stirring, pure equimolar solutions (0·05M) of $MgSO_4.7H_2O$ and $NH_4H_2PO_4$; the initial pH's were obtained by adding, prior to mixing, appropriate volumes of 1·5 M ammonia to the $NH_4H_2PO_4$ solution. Two crystals, to be employed for the polarity determination, were grown under the following initial conditions: crystal (1), $\beta = 20$, pH $=$ 6·9, 298 K; crystal (2): $\beta = 2{\cdot}8$, pH $= 6{\cdot}33$, 298 K, where $\beta = a(Mg^{2+})a(NH_3)a(HPO_4^-)/K_{sp}$(struvite) (for details and numerical values *cf.* Abbona, Lundager Madsen & Boistelle, 1982). A third crystal, to be used for an accurate refinement, was grown at: $\beta = 2{\cdot}5$, pH $= 6{\cdot}30$, 298 K. In this way we operated within a large range of fairly high supersaturations. The variations in crystal habit complied with former results on this topic (Abbona & Boistelle, 1979, and references therein). Special attention was paid to the relative extension of pedions {001} and {00$\bar{1}$}, particularly useful for controlling the crystal orientation

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on the diffractometer. In this respect we may note that crystal (1) showed $\{001\}$ well developed and $\{00\bar{1}\}$ much less extended, crystal (2) showed $\{001\}$ moderately developed whilst the complementary form was missing, crystal (3) showed $\{001\}$ well developed and $\{00\bar{1}\}$ very small; the other forms in order of decreasing importance were: $\{011\}$, $\{101\}$, $\{01\bar{2}\}$, $\{01\bar{1}\}$. Fig. 1 shows the forms of crystal (3) indexed according to the correct polarity.

Diffractometer measurements

Crystals (1) and (2) were employed for the measurements of an adequate number of Friedel pairs with a Nicolet *R*3 diffractometer using Cu $K\alpha$ radiation. To perform a more accurate refinement, Mo $K\alpha$ radiation was used with crystal (3) to collect a large number of independent reflexions. In all three cases the ω-scan technique was employed at variable speed; from 1·5° min^{-1} for the weakest to 10·0° min^{-1} for the strongest reflexions; scan range: 1·60°; left and right backgrounds measured in stationary mode for 0·8 times the peak-scan time. Two standard reflexions, monitored every fiftieth measurement: no decrease in the course of the measurement. Crystal (1): $0{\cdot}20\times 0{\cdot}12\times 0{\cdot}32$ mm, reciprocal-sphere octants *hkl* and $hk\bar{l}$ explored within $2\theta = 125°$; 771 reflexions measured, 767 with $I \geq 2\sigma(I)$ considered as observed and included in the analysis (*h*: 0–8; *k*: 0–7; *l*: −12–+12); 3 low-angle reflexions discarded in the course of the refinement because they were probably affected by the secondary-extinction effect. 723 Friedel pairs. Crystal (2): $0{\cdot}28\times 0{\cdot}18\times 0{\cdot}41$ mm, octants *hkl* and $hk\bar{l}$ explored within $2\theta = 130°$; 879 reflexions obtained, 872 observed; 820 Friedel pairs (*h*: 0–8; *k*: 0–7; *l*: −13–+13); Cu attenuator inserted for 19 intensities exceeding 60 000 counts s^{-1} on the pre-scan and 9 of these still had to be discarded because of poor F_o *vs* F_c agreement. Empirical absorption correction, based on the ψ-scan method (North, Phillips & Mathews, 1968) and four reflexions, $48° \leq 2\theta \leq 98°$; absorption coefficients 1·00 to 1·20. Crystal (3): $0{\cdot}20\times 0{\cdot}30\times 0{\cdot}45$ mm, $hk\bar{l}$ octant explored within $2\theta = 70°$; 1034 independent reflexions measured, 990 observed (*h*: 1–8; *k*: 0–9; *l*: $\bar{1}\bar{8}$–0). Only reflexion 004 had to be discarded. Absorption correction based on the ψ-scan method and four reflexions, $10{\cdot}7° \leq 2\theta \leq 35{\cdot}7°$; coefficients 1·005 to 1·143.

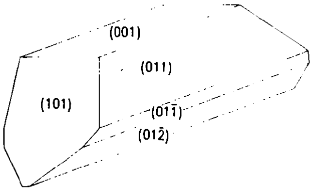

Fig. 1. Clinographic projecton of the forms of crystal (3) indexed according to the correct polarity.

Refinement and determination of the correct polarity

For all subsequent computations use was made of the *SHELXTL* system (Sheldrick, 1981). The coordinates of the non-hydrogen atoms obtained by WJ(*a*) were used as a starting model for the refinement based on standard least-squares methods. The H atoms were located on difference Fourier maps at an advanced stage of the anisotropic refinement (see *Results*). The scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974) and the anomalous-dispersion corrections for O, N, and Mg were introduced from the beginning. The origin was fixed by keeping constant, at 0·0005, the *z* coordinate of P. The positional parameters of the H atoms were refined under the following initial constraints using three different 'free variables' (Sheldrick, 1981). The N–H lengths were set equal to $0{\cdot}88 \pm 0{\cdot}005$ Å, FVAR1, and the H···H separations equal to FVAR1 × $1{\cdot}633 \pm 0{\cdot}005$ Å in order to ensure a tetrahedral arrangement around the N atom. The *W*–H(*i*, *j*) and H(*i*, 1)···H(*i*, 2) distances were similarly constrained to refine from $0{\cdot}95 \pm 0{\cdot}005$ Å, FVAR2, and $1{\cdot}48 \pm 0{\cdot}010$ Å, FVAR3, with no constraint between them to allow for more latitude of settlement. These starting values looked sensible and agree with those reported in the literature. The thermal parameters of the H atoms were set equal to 1·2 times the equivalent *U* values of the bonded atoms. In the case of crystal (2) unit weights proved satisfactory; in the final cycles of the other two refinements the following weighting scheme was introduced: $w = 1/[\sigma^2(F_o) + GF_o^2]$ where σ is the standard deviation of F_o, based on counting statistics, and *G* a variable to be adjusted after each cycle. Under the above conditions two parallel refinements were run with the data of both crystals (1) and (2): one based on the set of coordinates from WJ(*a*) and the other on the antipodal $1-x$, $1-y$, $1-z$ set (Sheldrick, 1981). At convergence (mean $\Delta/\sigma < 0{\cdot}04$) the following values of the agreement parameters were obtained for the former and latter set of coordinates respectively. Crystal (1): $R = 0{\cdot}0402$, 0·0322; $wR = 0{\cdot}0458$, 0·0332; $RG = 0{\cdot}0596$, 0·0430; goodness of fit = 2·283, 1·224; $G = 0{\cdot}00065$, 0·00126 for 764 reflexions and 98 parameters. FVAR1 = 0·90 (3), 0·89 (2); FVAR2 = 0·86 (2), 0·87 (2); FVAR3 = 1·37 (4), 1·39 (3) Å. Crystal (2): $R = 0{\cdot}0419$, 0·0331; $RG = 0{\cdot}0468$, 0·0378; goodness of fit = 0·798, 0·634 for 863 reflexions and 79 parameters; the coordinates of the H atoms of the water molecules were kept fixed in the closing cycles. FVAR1 = 0·91 (2), 0·92 (2); FVAR2 = 0·812 (4), 0·812 (4); FVAR3 = 1·351 (6), 1·351 (6).

The Hamilton test (*International Tables*, 1974; pp. 287–292; Rogers, 1981) favours the second polarity at the 0·005 confidence level and the scrutiny of the relative F_o, F_c values of the Friedel pairs confirms the choice. Besides, Rogers's (1981) parameter (see

Calleri, Gavetti, Ivaldi & Rubbo, 1984) refined to ±1·06 (7) for the correct and incorrect polarity respectively. Therefore, the correct polarity of struvite may be considered as established at a very high reliability level. With reference to the triad of axes of Figs. 1 and 2 and to that of WJ(*a*), the correct coordinates are those given in Table 1, obtained from the refinement based on the data collected with crystal (3). This third refinement was completed under the above conditions excepting that FVAR3 was set equal to 1·48 ± 0·005 Å. The correct and antipodal set of coordinates yielded at convergence (mean $\Delta/\sigma \leq 0{\cdot}01$) the following values. Crystal (3): $R = 0{\cdot}0286$, 0·0282; $wR =$ 0·0302, 0·0297; $RG = 0{\cdot}0364$, 0·0357; goodness of fit = 1·132, 1·127; $G = 0{\cdot}00062$, 0·00059 for 989 independent reflexions and 98 parameters; FVAR1 = 0·92 (2), 0·92 (2); FVAR2 = 0·80 (1), 0·80 (1); FVAR3 = 1·34 (2), 1·34 (2) Å. Here the deductions derivable from the *R* ratio are inconclusive (Rogers, 1981).*

Table 1. *Atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms,* $\times 10^3$ *for hydrogen atoms) and isotropic temperature factors* ($Å^2 \times 10^4$), *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}^* or U_{iso}
P	10000	10065 (1)	10005	143 (1)*
O(1)	10000	10220 (3)	1378 (2)	226 (5)*
O(2)	10000	2380 (2)	9465 (2)	218 (5)*
O(3)	8179 (2)	8863 (2)	9584 (1)	211 (3)*
Mg	10000	6232 (1)	6283 (1)	176 (2)*
W(1)	10000	3163 (3)	7137 (2)	376 (8)*
H(1, 1)	1000	305 (7)	785 (4)	449
H(1, 2)	1000	184 (7)	685 (4)	449
W(2)	10000	9214 (4)	5356 (3)	406 (8)*
H(2, 1)	897 (5)	986 (4)	503 (4)	489
W(3)	7825 (3)	7369 (2)	7382 (1)	265 (4)*
H(3, 1)	815 (5)	795 (4)	806 (3)	319
H(3, 2)	720 (4)	815 (5)	702 (3)	319
W(4)	7892 (2)	5147 (2)	5148 (2)	321 (5)*
H(4, 1)	768 (5)	387 (2)	512 (3)	385
H(4, 2)	702 (4)	590 (3)	493 (3)	385
N	10000	6341 (5)	2673 (3)	332 (8)*
H(1)	1000	761 (3)	224 (3)	397
H(2)	1000	666 (5)	348 (2)	397
H(3)	895 (3)	551 (3)	248 (2)	397

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results

Tables 1 and 2 give the final parameters and relevant distances and angles obtained from the more accurate ($R = 0{\cdot}0286$) third refinement using the coordinates for the correct polarity previously established. There is no significant difference between bond distances and angles based on the two sets of coordinates in all three cases. The values obtained from the refinements based on Cu *Kα* diffractometry do not differ from those of Table 2 by more than two or three times the e.s.d.'s there reported.† The mean values of Table 2 are unweighted and the bond distances are uncorrected for the libration effect; at any rate the in-phase libration corrections were not significant. For a detailed description of the structure and its hydrogen-bonding net, the reader is referred to WJ(*a*).

All H atoms were located on difference Fourier maps and in the case of the third refinement the heights of the peaks corresponding to the H atoms of the water molecules ranged from 0·54 to 0·45 e $Å^{-3}$. The distribution of residual electron density around N was neat and showed two peaks [H(1) 0·44 and H(2) 0·34 e $Å^{-3}$], coplanar with N, on the mirror plane orthogonal to the *x* axis, and two others in general positions related by the mirror plane itself [H(3) 0·35 e $Å^{-3}$] as it obtains with the phosphate-group O atoms (Fig. 2, Table 2). This model refined smoothly and the final difference map showed no ripples, except those associated with P and Mg (height ~ 0·25 e $Å^{-3}$). The refinements based on Cu *Kα* diffractometry yielded similar results. Hence, within the chosen experimental conditions, the postulate of disorder for the ammonium ion does not seem necessary, contrary to the findings of WJ(*a*, *b*). The ion is in the form of a fairly regular tetrahedron. The PO_4 tetrahedron is remarkably regular (Table 2) and reveals an appreciable π-bond character equally divided among the four bonds (*e.g.* Calleri & Speakman, 1964, and references therein).

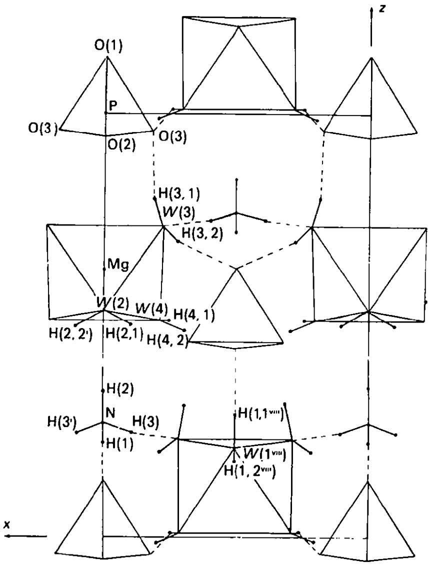

Fig. 2. Projection of the unit-cell contents along [010].

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*Lists of structure factors and anisotropic thermal parameters and the results for the electrostatic balance have been deposited with the British Library Lending Division as Supplementary Publication No. SUP39141 (10pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

†The results from the two refinements based on Cu *Kα* diffractometry are available from the authors.

Table 2. *Bond lengths* (Å) *and angles* (°)

Phosphate tetrahedron; e.s.d.'s in parentheses

P–O(1)	1·543 (2)	O(1)–P–O(2)	109·5 (1)
P–O(2)	1·546 (2)	O(1)–P–O(3)	109·6 (1)
P–O(3)	1·542 (1)	O(2)–P–O(3)	108·7 (1)
Mean	1·544 (1)	O(3)–P–O(3^i)	110·7 (1)
		Mean	109·6 (1)
O(1)–O(2)	2·523 (3)		
O(1)–O(3)	2·521 (2)		
O(2)–O(3)	2·509 (2)		
O(3)–O(3^i)	2·537 (3)		
Mean	2·522 (2)		

Mg. $6H_2O$ octahedron; e.s.d.'s in parentheses

Mg–*W*(1)	2·115 (1)	*W*(1)–Mg–*W*(3)	91·8 (1)
Mg–*W*(2)	2·106 (3)	*W*(1)–Mg–*W*(4)	89·5 (1)
Mg–*W*(3)	2·075 (2)	*W*(2)–Mg–*W*(3)	90·0 (1)
Mg–*W*(4)	2·054 (2)	*W*(2)–Mg–*W*(4)	88·6 (1)
Mean	2·087 (2)	*W*(3)–Mg–*W*(3^i)	93·8 (1)
		W(3)–Mg–*W*(4)	87·4 (1)
W(1)–*W*(3)	3·007 (3)	*W*(4)–Mg–*W*(4^i)	91·3 (1)
W(1)–*W*(4)	2·935 (3)	Mean	90·3 (1)
W(2)–*W*(3)	2·957 (3)		
W(2)–*W*(4)	2·907 (3)		
W(3)–*W*(3^i)	3·030 (3)		
W(3)–*W*(4)	2·853 (2)		
W(4)–*W*(4^i)	2·936 (3)		
Mean	2·946 (1)		

Hydrogen-bonding scheme; e.s.d.'s are 0·002–0·003 Å and 0·1° for distances and angles between O atoms, 0·02–0·04 Å and 1°–4° for distances and angles involving H atoms

A	*B*	*C*	*D*	*E*	*AB*	*BC*	*AC*	*CE*	*CD*	*DE*	*BCD*	*ABC*	*CDE*	*ACE*
O(2)	···H(1,1)–	*W*(1)	–H(1,2)···	*W*(2^{ii})	1·85	0·81	2·655	3·144	0·87	2·33	106	172	155	
O(3^{iii})	···H(2,1)–	*W*(2)	–H(2,1^i)···	O(3^{iv})	1·76	0·90	2·656	2·656	0·90	1·76	106	172	172	113·0
O(3)	···H(3,1)–	*W*(3)	–H(3,2)···	O(1^v)	1·80	0·87	2·646	2·708	0·77	1·97	110	164	163	105·4
O(3^{vi})	···H(4,1)–	*W*(4)	–H(4,2)···	O(2^{vii})	1·88	0·80	2·651	2·637	0·80	1·84	114	161	178	104·5
W(3^{viii})	···H(3)				2·16	0·92	3·028				110	157		125·9
		N	–H(1)···	O(1)				2·790	0·92	1·87			179	
W(4^i)	···H(2)				2·56	0·92	3·226				110	130		

Superscripts refer to the equivalent positions: (i) $2-x, y, z$; (ii) $x, y-1, z$; (iii) $1·5-x, 2-y, z-0·5$; (iv) $0·5+x, 2-y, z-0·5$; (v) $0·5+x, 2-y, 0·5+z$; (vi) $1·5-x, 1-y, z-0·5$; (vii) $x-0·5, 1-y, 0·5+z$; (viii) $0·5-x, 1-y, z-0·5$.

Discussion

Behaviour of NH_4^+; *electrostatic balance*

Three of the H atoms of this group, H(1), H(3) and H(3^i), form hydrogen bonds (Table 2). The fourth, H(2), is 2·56 (3) Å from *W*(4) and *W*(4^i) and the corresponding *W*–H···N angles are 130 (2)°; therefore, these interactions cannot be considered true hydrogen bonds, but contribute to clamping in position the ammonium ion and to achieving electrostatic balance. Within the first coordination sphere the ion is surrounded by five O atoms: O(1), *W*(3), *W*(3^i) and, at larger distances, *W*(4), *W*(4^i). The coordination is then strictly reminiscent of that of K^+ in the struvite analogue $MgKPO_4.6H_2O$ (Mathew & Schroeder, 1979). The coordination cavity is a very prolate spheroid. It may be noted that a range of N···O distances (2·79–3·23 Å, Table 2) meets coordination number (CN) 5 according to the survey by Khan & Baur (1972). A small CN (from 4 to 5) in its turn favours the hydrogen-bonding tendency of NH_4^+ to prevail over its pseudo-alkali character displayed with large CN (7 to 9). All this agrees with an ordered configuration of this group.

The electrostatic balance, calculated exploiting the Brown & Shannon (1973) relationships with appropriate parameters, shows that O(1) and *W*(2) are underbalanced to the same extent ($\sum s_i = 1·86$ instead of 2·00). However, the underbonding of O(1) agrees with the tendency for NH_4^+ ions with small CN's to be bonded to slightly undersaturated O anions (Khan & Baur, 1972), whilst *W*(2) may receive a small further contribution from NH_4^+ [Fig. 2; *W*(2)···H(2) = 2·63 (3) Å, *W*(2)···H(2)–N = 155 (2)°]. The detailed results have been deposited.

Surface features and growth rates

The correct polarity being known, the more likely surface structures of any form of struvite crystals can be deduced applying the Hartman & Perdok (1955) periodic bond chain (PBC) method [*cf.* also the preceding paper on epsomite (Calleri *et al.*, 1984). The outstanding morphologic zone of struvite crystals is [100]; Fig. 3 is the projection of the structure along this axis. It displays the shape of the most likely among the PBC's which can be singled out along [100] and shows the surface structures of the common forms {001}, {011}, {01$\bar{2}$} and of their complementary ones. The PBC chosen by us along [100] can be connected to its symmetry equivalent along [010] and [0$\bar{1}$1], which are also PBC directions (Abbona & Boistelle, 1979), to yield slices of thickness d_{002} and d_{011} respectively. The faces of {001} and {011}, of type *F* after Hartman & Perdok (1955), are more developed than those of the complementary {00$\bar{1}$} and {0$\bar{1}\bar{1}$} forms as we could clearly notice on our crystals. The effect is due to the different growth rates of the opposite faces relatable to their different surface structures. In fact, at the outermost layers of (001) and (011), Fig. 3, there is a higher density of electropositive groups (NH_4, H) than at the layers of (00$\bar{1}$)

and $(0\bar{1}\bar{1})$ where a higher density of PO_4 groups obtains. This implies different activation energies for the desorption and desolvation processes from the opposite faces and consequently a different extension. The above effect may be strengthened or attenuated by the different electronic polarizability of the complementary surfaces (Monier & Kern, 1956, and references therein). Monier & Kern's (1956) theory, originally developed for growth in the gaseous state of noncentrosymmetric crystals, leads to the conclusion that the more polarizable of two complementary forms is the more favoured. The theory seems to hold its validity also in the present case of growth from solution, with all due reserve (*e.g.* Cadoret, 1965). In point of fact, only NH_4 groups outcrop on (001) and they are likely to be more polarizable than the PO_4 and $Mg(H_2O)_6$ groups emerging on $(00\bar{1})$, Fig. 3. Nonetheless this contribution should become determinant only when the difference between the activation energies of depolarization of two complementary forms [$\Delta P \simeq 4$ kJ mol^{-1}, as calculated by Cadoret (1965) and Cadoret & Monier (1967) for some ionic compounds] is greater than the corresponding difference between the dehydration or surface diffusion activation energies per bonding unit. The lack of calculated or experimental values does not allow us to draw semiquantitative conclusions on the effective role played by the surface depolarization on the relative development of complementary forms.

Form $\{01\bar{2}\}$ is usually well developed whilst its complementary $\{0\bar{1}2\}$ is never present. The stability of the former, which has an *S* character, may be accounted for on postulating a selective absorption of some component from the mother solution on the steps of *S* profile (Cadoret, 1965).

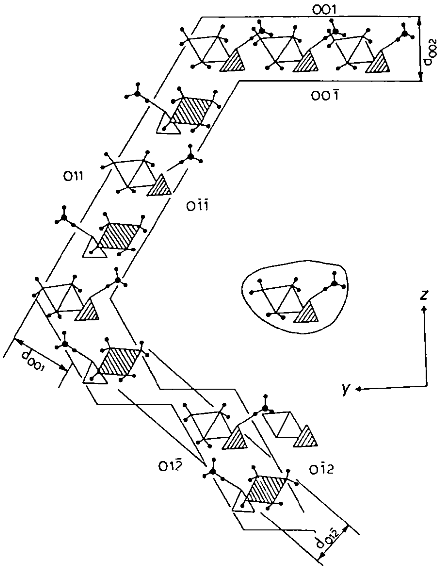

Fig. 3. Projection along $[\bar{1}00]$ of the structure. The profiles of the more common forms are displayed. The more likely [100] PBC is sketched inside.

It is necessary to emphasize that changes in the growth conditions, such as impurity concentration, pH, supersaturation, may even invert the relative size of faces belonging to the same pair of complementary forms (Cadoret & Monier, 1965). In the specific instance of struvite, crystals from the same natural source were found to exhibit different developments of (001) and $(00\bar{1})$ with size inversion (Kalkowsky, 1886). This may explain why arsenstruvite (Ferraris & Franchini-Angela, 1973) was found to show a polarity opposite to that found here for struvite. The arsenstruvite crystals were prepared (De Schulten, 1903) from solutions much more concentrated and acidic than ours; besides, they were rich in foreign ions ($[Na^+] \simeq 0{\cdot}6\,M$) and non-stoichiometric ($[As] \simeq 1{\cdot}5[Mg]$). These marked differences in the growth conditions affected the arsenstruvite crystal habit which is different from ours, being tabular according to {010}, with small {001}, {012}, {011} and {110} (Ferraris & Franchini-Angela, 1973). In conclusion, the crystal habit alone is not always a sufficient criterion for controlling the correct polarity of struvite. Other surface or bulk effects, such as etch pits and pyroelectricity respectively, are to be considered; research on this subject is in progress.

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