

formation, the other atoms undergo a displacive transition from one ordered arrangement to another. The discontinuity results from an adjustment of the H atoms to positions which are midway between the positions satisfying the stable configurations of each half of the twin. The function of the twinning is to minimize the overall shape changes that occur in the macroscopic crystal on the transformation from orthorhombic to monoclinic symmetry.

It is interesting to compare the structure of this phase transition with that of  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  (Chapuis, Arend & Kind, 1975). Comparison of the above results with the corresponding table in Chapuis *et al.* shows certain similarities (however, these are not very great).  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  shows evidence of disorder of some of the H atoms, but  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ , as noted above, shows no disorder at all. Thus the tetragonal symmetry of the crystals with Cd could be because of a random distribution, while in the Mn compound it is a result of twinning. An alternative explanation of why  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  shows disorder and  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  does not may be related to the fast rotation of  $\text{CH}_3$  groups, as well as to a small but real rotation of  $\text{NH}_3$  groups. This condition in the structure of  $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$  would further reduce the possibility of twinning.

We conclude that either  $(\text{CH}_3\text{NH}_3)$  as a whole or the H atoms alone are important factors in allowing or pre-

venting the introduction of the disordered or twinned state.

Support of this research by the Bundesminister Für Forschung und Technologie and the Institute for Crystallography, Tübingen University, is gratefully acknowledged.

#### References

- BACON, G. E. (1962). *Neutron Diffraction*. Oxford Univ. Press.
- CHAPUIS, G., AREND, H. & KIND, R. (1975). *Phys. Stat. Sol.* **31**, 449.
- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT. Oxford: Pergamon Press.
- FRIEDEL, G. (1905). *Bull. Soc. Industr. min. St. Etienne*, **4**, 563.
- HEGER, G., MULLEN, D. & KNORR, K. (1976). *Phys. Stat. Sol.* In the press.
- KNORR, K., JAHN, I. R. & HEGER, G. (1974). *Solid State Commun.* **15**, 231–238.
- MIKHAIL, I. (1977). To be published.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- PETZELT, J. (1975). *J. Phys. Chem. Solids*, **33**, 1005–1014.
- STEWART, J. M. (1967). The X-RAY 67 system. Tech. Rep. TR-67-58. Computer Science Center, Univ. of Maryland, College Park, Maryland.

*Acta Cryst.* (1977). **B33**, 1321–1325

## A Study of the Crystal Structure of $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ by Neutron Diffraction at 404 K

By I. MIKHAIL

*Institut für Kristallographie der Universität Tübingen, Germany (BRD)*

(Received 2 September 1976; accepted 6 October 1976)

The 404 K phase transition in  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  involves a change from the face-centred orthorhombic room-temperature structure to a tetragonal structure, space group  $I4/m$ , with  $a = b = 5.119$ ,  $c = 19.48$  Å and  $Z = 4$ . This high-temperature cell is related to the orthorhombic cell by  $a_{\text{tet}} = |110|/2$  and  $c_{\text{tet}} = c_{\text{orth}}$ . The crystal structure has been determined by neutron diffraction (wavelength 1.0346 Å). Full-matrix least-squares refinement resulted in a final  $R$  of 5.6% for 133 reflexions. The  $(\text{CH}_3\text{NH}_3)^+$  cation shows orientational disorder and is arranged in zigzags in order to retain tetragonal symmetry. The crystal is governed by the behaviour of the  $(\text{CH}_3\text{NH}_3)$  group which gives rise to the hydrogen-bond system in the structure. The intramolecular hydrogen bonds may be considered as principally responsible for the twisting of the  $\text{MnCl}_6$  octahedra. A weak  $\text{C}-\text{H} \cdots \text{Cl}$  bifurcated hydrogen bond is present.

#### Introduction

This work is part of a systematic study of  $(\text{C}_n\text{H}_{2n-1}\text{NH}_3)_2\text{MCl}_4$ , where  $M = \text{Mn, Fe or Cu}$ . The study of  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  has previously been at-

tempted by Foster & Naida (1968) and Peterson & Willet (1972). On the basis of the indexing of powder photographs, the unit cell was believed to be tetragonal, similar to that of  $\alpha\text{-Cs}_2\text{MnCl}_4$ . The existence of the phase transition has been established by optical obser-

vations and X-ray analysis (Knorr, Jahn & Heger, 1974). They show that the crystal is orthorhombic at room temperature. Above this temperature (at 393.8 K) the crystal possesses tetragonal symmetry. Below room temperature the symmetry changes to tetragonal (at 256.9 K) and finally to monoclinic (95.1 K). The space group  $I4/mmm$  was assigned to the high tetragonal phase by Heger, Mullen & Knorr (1975). Examination of diffraction data for characteristic extinctions showed that the positions of diffraction maxima were in accord with  $4/mmm$  ( $D_{4h}^{17}$ ); however, the intensities of symmetry-related reflexions showed marked inconsistencies with this diffraction symmetry. The space group  $I4/m$  was chosen. Because the author considered space group  $I4/mmm$  unlikely and because of continuing interest in this Institute in the role of the hydrogen bond, it was thought worthwhile to reinvestigate the structure in space group  $I4/m$ , in order to obtain more reliable structural features.

#### Unit cell and space group

Unit-cell dimensions and other crystallographic data at 404 K are: tetragonal, space group  $I4/m$ ,  $a = b = 5.119$ ,  $c = 19.48$  Å,  $Z = 2$ . Optical property: uniaxial negative.

The data show the diffraction symmetry  $I4/mmm$ . As the correct space group cannot be uniquely determined from the systematic absences, the restrictions on the study of the intensities were of importance. As the only systematic absences observed are those of reflexions for which  $h + k + l$  is odd, the lattice is established as body-centred tetragonal, and the possible space groups are  $I4/mmm$ ,  $I4_2m$ ,  $I\bar{4}m2$ ,  $I4mm$ ,  $I422$ ,  $I4/m$ ,  $I\bar{4}$  and  $I4$ .

The relationships  $I_{hkl} \neq I_{\bar{h}kl}$  and  $I_{hkl} = I_{h\bar{k}l}$  eliminated the first five space groups with the same systematically absent reflexions. The centrosymmetric space group  $I4/m$  was chosen. This was supported by the good correspondence between the experimental 'E' distributions and those expected theoretically for a centrosymmetric space group (Table 1).

Table 1. Experimental and theoretical statistical distributions of the normalized structure factor  $E$

	Experimental	Centro-symmetric	Noncentro-symmetric
$\langle  E ^2 \rangle$	1.0	1.0	1.0
$\langle  E^2 - 1  \rangle$	0.997	0.968	0.736
$\langle  E  \rangle$	0.804	0.798	0.886
$ E  > 3$	0.2%	0.2%	0.01%
$ E  > 2$	5.3	4.5	1.8
$ E  > 1$	32.2	31.7	36.8

#### Intensity data

The neutron intensity data were measured on a P32 neutron diffractometer at the FR2 reactor in Karlsruhe. The neutron wavelength was 1.0327 Å. The crystal used was an irregular platelet on (001). The measured intensity values were assigned the observational variance  $\sigma^2(I)$  according to the statistics of the scan and background counts plus an additional term (0.03  $S$ ,  $S$  being the scan count). The same intensity data (measured by G. Heger) have been used in the present analysis. It was noted that all reflexions with  $l = 2n + 1$  were relatively weak.

#### Structure determination and refinement

From the fact that all  $l = 2n + 1$  reflexions are weaker relative to those with  $l = 2n$ , the position 8(h) could be eliminated. Thus, by placing Cl(1) on the general position (with occupancy  $\frac{1}{4}$ ), Cl(2) on the position 8(g) (with a half occupancy) and Mn at (000) on 2(a), all predicted Cl—Cl and Mn—Cl vector positions and peak heights were in excellent agreement with the Patterson map. A structural calculation for the Mn and Cl atoms of the trial model gave an  $R$  of 32%. A three-dimensional Fourier synthesis was then computed with the signs based on the contributions of the atoms. The electron density map showed all the N and C atoms in general positions, both with half occupancy. At this stage the  $R$  value was 22% for all reflexions (excluding the zero reflexions). Positional parameters and individual isotropic temperature factors, as well as the single scale factor, were refined with modified versions of the full-matrix least-squares program of Busing, Martin & Levy (1962). After three cycles of refinement the  $R$  index dropped to 14.9%.

At this stage a three-dimensional  $F_o - F_c$  map was calculated to obtain information on the positions of the H atoms. The positions of H(1) and H(2) attached to N were clearly revealed, with an occupancy of  $\frac{3}{8}$  for each position, but the remaining H atoms were poorly visible. A new difference map based on calculated structure factors, including atoms H(1) and H(2), still gave poorly resolved peaks for the H atoms attached to C atoms. However, it was possible to obtain approximate coordinates for all the remaining H atoms from this map if it was assumed that they were situated at positions with  $C - H \approx 1.08$  Å. At this stage all the H atoms were included in the calculation of the structure factors. During the refinement it was necessary to reduce the occupancy factor for H(3) from  $\frac{3}{8}$  to  $\frac{1}{4}$  and to increase the occupancy factor of H(4) from  $\frac{3}{8}$  to  $\frac{1}{2}$ , in order to obtain satisfactory agreement between observed and calculated values.  $R$  was reduced to 8.7%. Finally, least-squares refinement of positional and anisotropic thermal parameters for all H atoms and isotropic thermal parameters for Mn, Cl, C and N was carried out.

Table 2. Atomic parameters ( $\times 10^4$ , except  $B$ )

Positional parameters are given as fractions of the lattice translations. Anisotropic and isotropic temperature factors correspond to  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$  and  $T = \exp(-B \sin^2\theta/\lambda^2)$  respectively. Estimated standard deviations are given in parentheses.

	$x$	$y$	$z$	$B$		$x$	$y$	$z$	$B$
Mn	0	0	0	2.157 (9)	C	341 (5)	704 (3)	3123 (1)	2.961 (3)
Cl(1)	0	5000	111 (1)	2.652 (5)	N	285 (9)	383 (8)	3838 (1)	3.514 (3)
Cl(2)	569 (8)	-73 (4)	1269	2.922 (3)					
	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
H(1)	1956 (5)	1238 (2)	3979 (6)	160 (5)	970 (3)	69 (4)	-204 (3)	-15	-109 (3)
H(2)	-936 (3)	772 (1)	4085 (5)	1840 (4)	198 (6)	45 (6)	292 (4)	-186 (3)	31 (4)
H(3)	1690 (4)	1521 (1)	3008 (1)	113	1598 (1)	77 (1)	-529 (2)	72 (5)	146 (3)
H(4)	-413 (1)	1753	2912 (2)	1197 (1)	3712	63 (1)	-1969 (1)	-127 (1)	292

The refinement stopped at an  $R$  value of 5.6%. As a check on the correctness of the structure a three-dimensional difference map was computed. The difference map showed no interpretable features above random background ripples.

All computer computations were performed with the X-RAY 67 system of programs (Stewart, 1967) modified at the University of Tübingen. The scattering lengths for cell atoms were taken from Bacon (1962);  $b_{\text{Mn}} = -0.387$ ,  $b_{\text{Cl}} = 0.990$ ,  $b_{\text{N}} = 0.940$ ,  $b_{\text{C}} = 0.665$  and  $b_{\text{H}} = -0.374$  (all  $\times 10^{-12}$  cm). The results given here are based on the refinement with unit weight for all observed reflexions. 133 observed reflexions were used during the refinement. Final positional and thermal parameters are listed in Table 2.\*

### Results and discussion

The  $R$  values ( $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ ) for the model of Heger, Mullen & Knorr (1975) (hereafter HMK) and for the present work are 8% and 5.6% respectively for 133 reflexions (unobserved reflexions omitted). In each case  $R$  is derived from the same parameters. However, its value is not necessarily an infallible guide (yet cannot be wrong); the difference between 5.6% and 8.0% is sufficient to indicate the correctness of the present analysis.

In order to retain tetragonal symmetry, the  $(\text{CH}_3\text{-NH}_3)^+$  cation must either rotate or show orientational disorder. Because of the asymmetry of the packing forces which would be introduced by the requirement of ordering for C and disordering for N as shown by HMK, it is expected that the C atoms must be displaced away from the special position. Ignoring such a

displacement would result in the thermal-parameter factor being abnormal. Thus in the work of HMK, the larger apparent thermal motion of the  $\text{CH}_3$  groups as a whole with respect to the  $\text{NH}_3$  groups could possibly indicate an incorrect choice of the true position.

The C and N atoms in the present work were refined with equal occupation (both in general positions with half occupancy). The isotropic thermal parameters are

Table 3. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ), with standard deviations in parentheses

Mn-Cl(1)	2.569	Cl(1)-Mn-Cl(2)	86.08 (2)
Mn-Cl(2)	2.491 (6)	N-C-H(4)	126.48 (14)
C-H(4)	0.779 (11)		
Average values			
C-N	1.464 (6)	C-N-H(1)	103.67 (7)
C-H(3)	0.970 (1)	C-N-H(2)	126.76 (8)
C-H(4)	1.06 (4)	N-C-H(3)	106.79 (11)
N-H(1)	1.07 (6)	N-C-H(4)	111.02 (12)
N-H(2)	0.911 (4)		

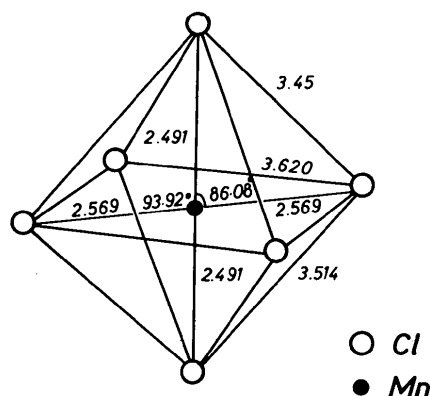


Fig. 1. The coordination around Mn.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32316 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

nearly equal and reasonable ( $B = 2.9$  and  $3.5 \text{ \AA}^2$  for C and N respectively). Thus, as expected, the absence of an abnormally high temperature factor implies that the displacement for C atoms is necessary and that the potential energy of the methyl group would be nearly the same on either side of the  $\text{NH}_3$  group. Some of the bond lengths and angles with the estimated standard deviations are listed in Table 3. With regard to the bond lengths and angles, the coordination around Mn is only slightly distorted octahedral. The Cl—Cl edge distances of the octahedron are  $3.45$  and  $3.54 \text{ \AA}$ . The Mn atoms are on a symmetry centre with paired internal angles  $\text{Cl}(1)\text{—Mn—Cl}(2)$   $86.08^\circ$  and  $\text{Cl}(2)\text{—Mn—Cl}(1)$   $84.35^\circ$ . The configuration of a single octahedron is shown in Fig. 1. The C—H bond lengths are in the range  $0.838$  to  $1.12 \text{ \AA}$  (mean  $0.974 \text{ \AA}$ ), except C—H(4)  $0.779 \text{ \AA}$ . The N—H distances are  $0.832$  to  $1.15 \text{ \AA}$  (mean  $0.998 \text{ \AA}$ ). The mean C—N bond length ( $1.476 \text{ \AA}$ ) is, however, in good agreement with the N—C single-bond length.

### Packing of the structure

The system of hydrogen bonds and the packing of the structure are shown in Fig. 2. Since some kind of interaction between Cl and H clearly exists, the  $\text{Cl} \cdots \text{H}$  dis-

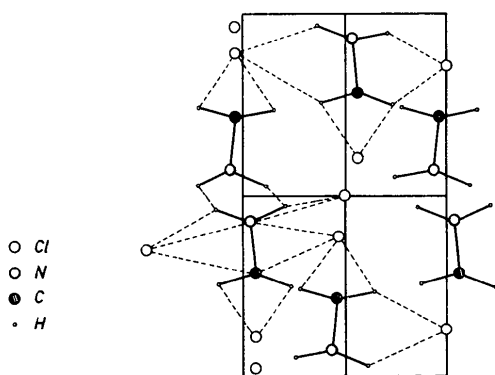


Fig. 2. Projection of the structure down  $b$ .

tances appear to be more important for the packing, or, more precisely, the packing is largely determined by the forces between the cation and the Cl ions. As seen in Table 4, some of the distances between Cl and H are in the range  $2.6$  to  $2.9 \text{ \AA}$ . These are shorter than the sum of the van der Waals radii ( $3.2 \text{ \AA}$ ). A hydrogen bond between Cl(2) and C seems a likely possibility in view of the polarity of the C—H(4) bond. On the assumption that the hydrogen-bond radius of CH is  $1.64 \text{ \AA}$  (Sax & Pletcher, 1969) and that the acceptor radius of the chloride ion is  $1.88 \text{ \AA}$ , the expected value for a  $\text{C} \cdots \text{Cl}^-$  hydrogen bond is  $3.54 \text{ \AA}$ . C is engaged in two contacts of this type with chloride ions. One of these distances is  $3.56 \text{ \AA}$  to a Cl(2) ion, with  $\text{H} \cdots \text{Cl}$   $3.17 \text{ \AA}$  and  $\text{C—H}(4) \cdots \text{Cl}(2)$   $99.94^\circ$ . The other distance is  $3.469 \text{ \AA}$  to Cl(2), with  $\text{H}(4) \cdots \text{Cl}(2)$   $3.066 \text{ \AA}$  and an angle of  $148.01^\circ$ .

The favourable orientation of  $\text{C} \cdots \text{H}(4)$  for the formation of a bifurcated hydrogen bond together with the C—Cl(2) distances make it reasonable to classify this interaction as a weak hydrogen bond. The range of  $\text{N} \cdots \text{Cl}$  contacts and  $\text{N—H} \cdots \text{Cl}$  angles is found to lie well within the ranges ( $3.15\text{--}3.51 \text{ \AA}$ ;  $122\text{--}180^\circ$ ) established by neutron diffraction for  $\text{NH—Cl}$  hydrogen bonds (Hamilton & Ibers, 1968).

Support for this research by the Bundesminister für Forschung und Technologie and the Institute for Crystallography, Tübingen University, is gratefully acknowledged.

### References

- BACON, G. E. (1962). *Neutron Diffraction*. Oxford Univ. Press.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.  
 FOSTER, J. J. & NAIDA, S. (1968). *J. Chem. Soc.* **54**, 2625.  
 HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids. Methods of Molecular-Structure Determination*. New York: Benjamin.  
 HEGER, G., MULLEN, D. & KNORR, K. (1975). *Phys. Stat. Sol. (a)*, **31**, 455.

Table 4. Some interatomic distances ( $\text{ \AA}$ ) and angles ( $^\circ$ ) with standard deviations in parentheses

$\text{C} \cdots \text{Cl}(2)^j$	3.283 (10)	$\text{N} \cdots \text{Cl}(1)^v$	3.465	$\text{H}(3) \cdots \text{Cl}(2)^i$	2.692 (12)	$\text{H}(1) \cdots \text{Cl}(1)^v$	2.773 (4)
$\text{C} \cdots \text{Cl}(2)^{ii}$	3.638 (9)	$\text{N} \cdots \text{Cl}(1)^i$	3.17	$\text{H}(3) \cdots \text{Cl}(2)^{ii}$	2.992 (11)	$\text{H}(2) \cdots \text{Cl}(2)^i$	2.634 (8)
$\text{C} \cdots \text{Cl}(2)^{iii}$	3.469 (9)	$\text{N} \cdots \text{Cl}(2)^i$	3.211	$\text{H}(4) \cdots \text{Cl}(2)^{iii}$	3.066 (11)	$\text{H}(1) \cdots \text{Cl}(2)^i$	2.386 (10)
$\text{C} \cdots \text{Cl}(2)^{iv}$	3.566 (11)	$\text{N} \cdots \text{Cl}(2)^{vi}$	3.455	$\text{H}(4) \cdots \text{Cl}(2)^{iv}$	3.178 (13)	$\text{H}(2) \cdots \text{Cl}(2)^{vi}$	2.863 (10)
$\text{C—H}(3) \cdots \text{Cl}(2)^i$	128.88 (8)	$\text{C—H}(4) \cdots \text{Cl}(2)^{iv}$	99.94 (8)	$\text{N—H}(2) \cdots \text{Cl}(2)^i$	123.58 (19)		
$\text{C—H}(3) \cdots \text{Cl}(2)^{ii}$	135.88 (7)	$\text{N—H}(1) \cdots \text{Cl}(1)$	126.80 (12)	$\text{N—H}(2) \cdots \text{Cl}(2)^{vi}$	129.73 (13)		
$\text{C—H}(4) \cdots \text{Cl}(2)^{iii}$	148.01 (8)	$\text{N—H}(1) \cdots \text{Cl}(2)^i$	139.37 (14)				

### Key to symmetry operations

(i)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$   
 (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$

(iii)  $x - \frac{1}{2}, \frac{1}{2} + y, \frac{1}{2} - z$   
 (iv)  $y - \frac{1}{2}, \frac{1}{2} - x, \frac{1}{2} - z$

(v)  $y, y, \frac{1}{2} + z$   
 (vi)  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$

- KNORR, K., JAHN, I. R. & HEGER, G. (1974). *Solid State Commun.* **15**, 231–238.
- PETERSON, E. R. & WILLETT, R. D. (1972). *J. Chem. Phys.* **56**, 1879.
- SAX, M. & PLETCHER, J. (1969). *Science*, **166**, 1546.
- STEWART, J. M. (1967). The X-RAY 67 system. Tech. Rep. TR-67-58. Computer Science Center, Univ. of Maryland, College Park, Maryland.

*Acta Cryst.* (1977). **B33**, 1325–1333

## The Crystal Structure of $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>\*

BY M. MATHEW,† L. W. SCHROEDER,† B. DICKENS AND W. E. BROWN‡

*Institute for Materials Research, National Bureau of Standards, Washington, DC 20234, USA*

(Received 19 August 1976; accepted 7 October 1976)

$\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> crystallizes in the monoclinic space group  $P2_1/a$  with  $a = 12.887(2)$ ,  $b = 27.280(4)$ ,  $c = 15.219(2)$  Å,  $\beta = 126.20(1)^\circ$ , and  $Z = 24$ . An approximate subcell with  $b' = b/3$  exists. The structure was solved by direct methods of phase determination and refined to  $R = 0.051$  and  $R_w = 0.049$  with 7002 reflections collected from a single crystal by counter methods. The structure consists of columns of cations, and columns of cations and anions with compensating cation vacancies, and is closely related to the structure of K<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>, the mineral glaserite. The calcium ions in  $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> exhibit a wide range of coordination numbers and geometries.

### Introduction

The chemistry of calcium phosphates is generally complex, and the phases with stoichiometry Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> provide no exception. A brief general description of these phases has been given in the paper on the crystal structure of pure  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (Dickens, Schroeder & Brown, 1974). The phase  $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is thermodynamically stable between 1120 and 1470°C (Fix, Heymann & Heinke, 1969) in the absence of impurities, but is metastable at room temperature. Here we report the determination of its crystal structure and discuss its place in the calcium phosphate family.

### Experimental methods and structure determination

Samples of  $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were made by heating pressed pellets of stoichiometric amounts of CaHPO<sub>4</sub> and

CaCO<sub>3</sub>, mixed with 1% cornstarch and a few drops of distilled water, to 1400°C for 2 d. Several crystals were ground into approximate spheres and mounted in random orientations on goniometer heads. A crystal with diameter 0.190(5) mm was mounted on a Picker§ four-circle diffractometer equipped with a highly oriented graphite monochromator and using Mo radiation. The cell dimensions were determined by least-squares refinement of  $2\theta$  values observed by automatically centering 30 reflections in the range  $48^\circ < 2\theta < 60^\circ$  [ $\lambda(\text{Mo } K\alpha_1) = 0.709260$  Å]. The diffractometer-controlling program was written by Lenhart (1975).

$\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> crystallizes in the monoclinic space group  $P2_1/a$ , with cell parameters  $a = 12.887(2)$ ,  $b = 27.280(4)$ ,  $c = 15.219(2)$  Å and  $\beta = 126.20(1)^\circ$  at 25°C. The calculated density for  $Z = 24$  of 2.863 g cm<sup>-3</sup> and the observed density of 2.81(1) g cm<sup>-3</sup> (Mackay, 1953) indicate some porosity, as expected for a sample prepared by a solid-state reaction between two different phases.

A prominent subcell exists with  $b'' = b/3$ , the cell reported by Mackay (1953). The real cell is shown by weak reflections for  $k \neq 3n$ . The metric symmetry is

\* This investigation was supported in part by Research Grant DE00572 to the American Dental Association Health Foundation from the National Institute of Dental Research, and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the American Dental Association.

† Research Associates, American Dental Association Health Foundation Research Unit at the National Bureau of Standards, Washington, DC 20234, USA.

‡ Director, American Dental Association Health Foundation Research Unit at the National Bureau of Standards, Washington, DC 20234, USA.

§ Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the NBS nor does it imply that the material or equipment identified is necessarily the best available for this purpose.