Acta Cryst. (1977). B33, 1812–1816

The Crystal Structure of Anhydrous Stannous Phosphate, $Sn_3(PO_4)_2$

By M. Mathew,* L. W. Schroeder* and T. H. Jordan†

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

(*Received* 23 *September* 1976; *accepted* 19 *November* 1976)

Anhydrous stannous phosphate, $Sn_3(PO_4)_2$, crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. The unit-cell parameters at 25°C are $a = 11{\cdot}092$ (8), $b = 4{\cdot}830$ (4), $c = 16{\cdot}401$ (10) Å and $\beta = 94{\cdot}28$ (5)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques to $R_w(F) = 0{\cdot}034$ and $R(F) = 0{\cdot}047$ with 1813 reflections. The structure consists of alternating layers of Sn^{II} and PO_4 ions parallel to the *ac* plane. Two open channels parallel to [010] are formed by Sn^{II} ions arranged in a helical fashion. Each Sn^{II} ion is at the apex of a trigonal pyramid with the three nearest O atoms, each from a different PO_4 group, forming the base. In one case, two Sn^{II} ions enter into a dimeric configuration by sharing an O···O edge of the pyramid. The corresponding Sn—O distances are 2·230(6) and 2·317(6) Å; the O—Sn—O angle of 69·6 (2)° is unusually small.

Introduction

Anhydrous stannous phosphate, $Sn_3(PO_4)_2$, was first reported as a product of the reaction of stannous chloride with hydroxyapatite (Collins, Nebergal & Langer, 1961; Collins, 1962). The compound has also been prepared by heating stannous oxide with either phosphoric acid or phosphorus pentoxide (Jordan, Gerrity & Hanusa, 1976).

A hydrated form, $Sn_3(PO_4)_2.3H_2O$, has been reported (Klement & Haselbeck, 1963). The powder diagram of this hydrated form is distinctly different from the powder diagram of $Sn_3(PO_4)_3$ (Collins, 1962).

This structure determination is part of a study in which we seek crystal-chemical information about products that may form in reactions between stannous compounds and tooth enamel.

Experimental

The crystal used in this study was obtained by heating a mixture of $Sn_3F_3PO_4$ and Sn_2FPO_4 that had been made by mixing 1 *M* solutions of SnF_2 and H_3PO_4. The crystal was approximately rectangular with dimensions 0·048 x 0·042 x 0·030 mm. Because of the rather irregular shape of this crystal, realistic absorption corrections could not be applied. Estimated values for the maximum and minimum transmission factors ($\mu = 88{\cdot}9$ cm^{-1}) are 0·82 and 0·63 respectively. The systematic absence of reflections *h*0*l* with $l = 2n + 1$ and 0*k*0 with $k = 2n + 1$ showed the space group to be $P2_1/c$. The crystal data at room temperature are: $a = 11{\cdot}092$ (8), $b = 4{\cdot}830$ (4), $c = 16{\cdot}401$ (10) Å, $\beta = 94{\cdot}28$ (5)°, $D_c = 4{\cdot}138$ g cm^{-3}, $V = 876{\cdot}2$ Å^3, FW 546·0, $F(000) = 976$, $Z = 4$.

The cell dimensions and standard deviations were obtained from least-squares refinements of 20 2θ values obtained by automatically centering reflections on a four-circle diffractometer equipped with a graphite monochromator. Mo $K\alpha_1$ ($\lambda = 0{\cdot}70930$ Å) radiation was used. The diffractometer-controlling program was written by Lenhert (1975).

X-ray intensity data were collected with θ–2θ scans. The 2θ scan rate was 1° min^{-1} and backgrounds were counted for 20 s at both ends of the scan range. All reflections in the hemisphere ($\pm hk \pm l$) up to $2\theta = 80°$ were measured, thus giving at least two measurements for each unique reflection. Three standard reflections were measured at intervals of 50 as a check of variation in intensity with time for scaling purposes. The data were averaged into a unique set of 1985 reflections, of which 1813 had observable intensity $[I \geq 2\sigma(I)]$ and were used in the least-squares refinements. Equivalent reflections agreed within 10% on the average (based on F^2).

Structure determination and refinement

The structure was solved by the heavy-atom method. The positions of two Sn atoms were readily deduced from a sharpened, three-dimensional Patterson synthesis. Although the third Sn atom position could also be obtained from the Patterson map, it was actually taken from a Fourier synthesis phased with two Sn

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

† Permanent address: Cornell College, Department of Chemistry, Mount Vernon, Iowa, 52314, USA.

Table 1. *Fractional coordinates and thermal parameters*

The figures in parentheses are the estimated standard deviations. The positional parameters are multiplied by 10^5 for the Sn atoms and by 10^4 for the remaining atoms. The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, and are multiplied by 10^4 for the Sn and P atoms and by 10^3 for the O atoms.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	80055 (6)	25527 (16)	28333 (4)	108 (3)	137 (3)	173 (3)	−10 (3)	6 (3)	−17 (3)
Sn(2)	47898 (7)	22053 (16)	13615 (4)	183 (4)	174 (4)	173 (3)	−3 (4)	4 (3)	−2 (3)
Sn(3)	14388 (7)	37016 (14)	46117 (5)	172 (3)	141 (3)	165 (3)	2 (4)	19 (2)	−20 (4)
P(1)	239 (2)	2891 (5)	1480 (1)	132 (11)	67 (12)	88 (10)	−5 (10)	2 (9)	−17 (11)
P(2)	6485 (2)	1949 (5)	4742 (2)	108 (12)	94 (13)	217 (14)	11 (11)	12 (11)	−25 (11)
O(11)	1295 (6)	1610 (12)	1979 (4)	16 (4)	7 (3)	19 (3)	0 (3)	−3 (3)	−2 (3)
O(12)	156 (6)	1778 (13)	592 (3)	14 (3)	9 (4)	13 (3)	3 (3)	5 (3)	−2 (3)
O(13)	−995 (6)	2146 (14)	1788 (4)	17 (3)	12 (4)	15 (3)	−5 (3)	8 (3)	−1 (3)
O(14)	442 (6)	6033 (14)	1481 (4)	17 (4)	9 (3)	14 (3)	−1 (3)	−3 (3)	−2 (3)
O(21)	7753 (6)	3113 (14)	4610 (4)	13 (4)	21 (4)	36 (4)	−6 (3)	5 (3)	−11 (4)
O(22)	5524 (6)	3260 (13)	4148 (4)	17 (4)	11 (4)	25 (4)	−2 (3)	−5 (3)	−4 (3)
O(23)	6239 (6)	2374 (16)	5636 (4)	15 (3)	26 (4)	24 (4)	2 (4)	2 (3)	−9 (4)
O(24)	6495 (6)	−1194 (14)	4539 (4)	9 (3)	11 (3)	35 (4)	3 (3)	−4 (3)	0 (4)

atoms. The remaining atoms were located in subsequent Fourier syntheses.

The refinement was carried out by full-matrix least-squares calculations with the program *RFINE*4 (Finger & Prince, 1975). The quantity minimized in the least-squares calculations was $\Sigma\, w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_{\rm ave})]^{-2}$. $\sigma^2(F_{\rm ave})$ is taken as $\Sigma_{i=1}^n \sigma_c^2(F_i)/n$ if it is greater than $\Sigma_{i=1}^n (F_i - F_{\rm ave})^2/(n-1)$, where n is the number of equivalent reflections; otherwise it is the average of the two estimates. Scattering factors for all atoms were those for the neutral atoms taken from *International Tables for X-ray Crystallography* (1974). Two cycles of least-squares calculations with individual isotropic temperature factors led to an R $(= \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|)$ of 0·068 and an R_w $\{= [\Sigma\, w(F_o - F_c)^2/\Sigma\, wF_o^2]^{1/2}\}$ of 0·044. Two additional cycles of refinement with anisotropic thermal parameters for all atoms reduced R to 0·047 and R_w to 0·034 (the corresponding values for all 1985 reflections are 0·058 and 0·036 respectively). The refinement was terminated with an average shift/error in the last cycle of 0·1 and a maximum value of 0·47. There were no abnormal correlation coefficients [−0·40 between β_{13} of Sn(1) and β_{13} of Sn(2) was the largest]. No allowance for extinction was found necessary. The final atomic parameters are listed in Table 1.*

Results and discussion

The crystal structures of $Sn_3(PO_4)_2$ and $SnSO_4$ (Donaldson & Puxley, 1972) provide an opportunity to see how the packing of Sn^{II} ions and XO_4 ions varies with the cation-to-anion ratio. The overall molecular packing is illustrated in Fig. 1. The two fairly large open channels at $x = \frac{1}{2}$ that run parallel to the b axis are formed by Sn atoms arranged in a helical fashion. Similar open channels have been noticed in other Sn^{II} compounds, *e.g.* $NaSn_2F_5$ (McDonald, Larson & Cromer, 1964), $Sn_3F_3PO_4$ (Berndt, 1972), $Sn_3O(OH)_2SO_4$ (Davies, Donaldson, Laughlin, Howie & Beddoes, 1975), and Sn_2OHPO_4 (Jordan, Schroeder, Dickens & Brown, 1976). Such open spaces are generally con-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32340 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

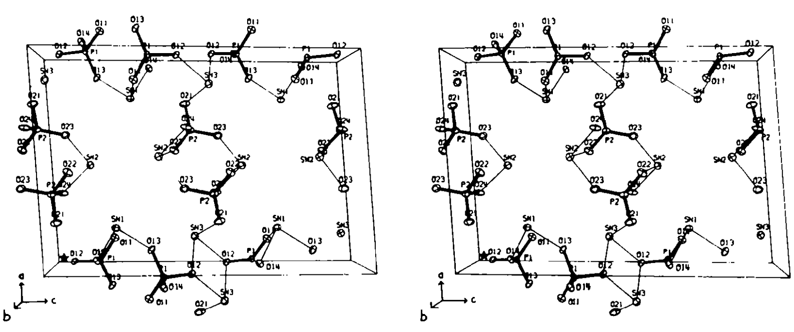

Fig. 1. A stereoscopic view of the unit cell of $Sn_3(PO_4)_2$. The origin of the coordinate system is marked by an asterisk.

sidered to be a result of the hemispherical coordination preferred by Sn^{II} ions. As in the case of $SnSO_4$, the basic coordination of Sn^{II} can be clearly ascertained from the observation (see Table 2) that three Sn—O distances are much shorter than the others. This eliminates the need for choosing a cut-off distance as a means of distinguishing between bonds of strong and intermediate strength.

The details of the coordination about Sn(1) and Sn(2) are shown in Fig. 2(*a*) and (*b*). Sn(1) is strongly coordinated to three O atoms from three different $P(1)O_4$ groups (average Sn—O distance 2·119 Å). The Sn atom is at the apex of a trigonal pyramid with the three O atoms at the base. The coordination around Sn(1) is completed by two additional weak contacts (average Sn—O distance 2·971 Å).

The primary coordination around Sn(2) is quite similar to that of Sn(1). There are three strong Sn···O bonds (average distance 2·100 Å) from three different $P(2)O_4$ groups. Again, Sn and the bonding O atoms form a trigonal pyramid. The only other Sn···O contact, Sn(2)—O(22), is at a distance of 3·054 Å.

The Sn—O distances and O—Sn—O angles (see Table 2) for Sn(1) and Sn(2) that make up the primary coordination geometry are quite similar to those observed in a wide variety of Sn^{II} compounds (for surveys see Jordan, Schroeder, Dickens & Brown, 1976; McDonald, Hau & Eriks, 1976).

The O—Sn—O angles average 10° larger than the corresponding ones in $SnSO_4$. In $SnSO_4$, nine weakly bonded O atoms surround each Sn in addition to the three strongly bonded O atoms. In $Sn_3(PO_4)_2$, the number of weakly bonded O atoms to Sn(2) and Sn(1) are one and two respectively. This suggests that the additional O···O repulsions in $SnSO_4$ may tend to compress the primary coordination geometry of Sn^{II}.

Table 2. *Bond angles* (°) *in* $Sn_3(PO_4)_2$

Sn environment	
O(11)—Sn(1)—O(13)	89·8 (2)
O(11)—Sn(1)—O(14)	88·2 (2)
O(13)—Sn(1)—O(14)	86·8 (2)
O(22)—Sn(2)—O(23)	88·5 (3)
O(22)—Sn(2)—O(24)	88·3 (3)
O(23)—Sn(2)—O(24)	94·2 (3)
O(21)—Sn(3)—O(12)	84·9 (2)
O(21)—Sn(3)—O(12')	84·8 (2)
O(12)—Sn(3)—O(12')	69·6 (2)
PO_4 groups and environment	
O(11)—P(1)—O(12)	110·8 (4)
O(11)—P(1)—O(13)	113·6 (4)
O(11)—P(1)—O(14)	107·3 (4)
O(12)—P(1)—O(13)	103·7 (4)
O(12)—P(1)—O(14)	110·0 (4)
O(13)—P(1)—O(14)	111·5 (4)
O(21)—P(2)—O(22)	111·0 (4)
O(21)—P(2)—O(23)	108·5 (4)
O(21)—P(2)—O(24)	107·7 (4)
O(22)—P(2)—O(23)	113·0 (4)
O(22)—P(2)—O(24)	106·5 (4)
O(23)—P(2)—O(24)	110·0 (4)
P(1)—O(11)—Sn(1)	135·9 (4)
P(1)—O(12)—Sn(3)	135·6 (4)
P(1)—O(12)—Sn(3')	110·7 (4)
P(1)—O(13)—Sn(1)	141·0 (4)
P(1)—O(14)—Sn(1)	117·2 (4)
P(2)—O(21)—Sn(3)	121·5 (4)
P(2)—O(22)—Sn(2)	135·9 (4)
P(2)—O(23)—Sn(2)	139·9 (4)
P(2)—O(24)—Sn(2)	119·4 (4)

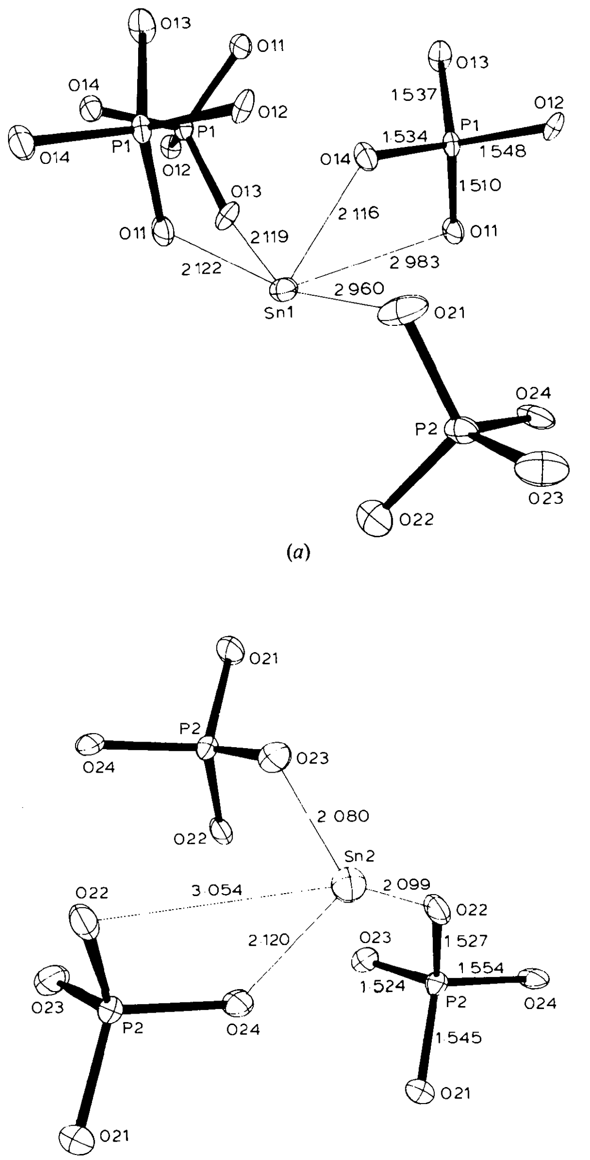

Fig. 2. (*a*) The environment of Sn(1) in $Sn_3(PO_4)_2$. (*b*) The environment of Sn(2). Standard deviations for the distances given are 0·007 Å.

The coordination around Sn(3) is different from those of the other two Sn atoms. The trigonal coordination is maintained, $\bar{d}$(Sn—O) = 2·231 Å, but there are three weaker bonds, $\bar{d}$(Sn—O) = 2·888 Å, and one very weak bond (3·250 Å). The salient feature of this coordination is the oxygen-bridged Sn(3)···Sn(3) dimer lying across a center of symmetry (Fig. 3). The unusually small angle, O(12)—Sn(3)—O(12') = 69·6 (2)°, may be a result of the bridge formation. The small O—Sn—O angle and the Sn···O bond distances of 2·230 and 2·317 Å, the longest ones in the primary coordination of Sn^{II} in $Sn_3(PO_4)_2$, indicate that Sn···Sn repulsion plays an important part in determining the dimeric configuration observed here. Such dimers have also been found in $NaSn_2F_5$ (McDonald, Larson & Cromer, 1964). As is the case with the other Sn atoms in this structure, the hemispherical coordination is maintained; the open side near the channel formed by Sn(1) and Sn(2) is presumably the site of the lone pair of electrons on Sn(3).

Fig. 1 also shows that the Sn^{II} and PO_4 ions form alternating layers parallel to the *bc* plane. The $P(1)O_4$ group layers can be thought of as made up of zigzag chains of PO_4 groups parallel to the *c* axis. Layers of $P(1)O_4$ groups are linked to layers of $P(2)O_4$ ions by Sn(3). Planes parallel to (100) might show cleavage because only one strong bond, Sn(3)···O(21), needs to be broken in separating the layers.

Although $Sn_3(PO_4)_2$ is a product of the reaction of stannous ions with hydroxyapatite, its crystal structure shows no significant relationship to that of $Ca_5(PO_4)_3OH$ (Kay, Young & Posner, 1964). This suggests that $Sn_3(PO_4)_2$ is unlikely to be formed as a crystalline overgrowth on hydroxyapatite upon reaction with stannous ions. In fact, the structure of $Sn_3(PO_4)_2$ seems more related to those calcium phosphates that have layers of PO_4 groups alternating with calcium ions and water molecules, *e.g.* $Ca(H_2PO_4)_2.H_2O$ (Schroeder, Prince & Dickens, 1975).

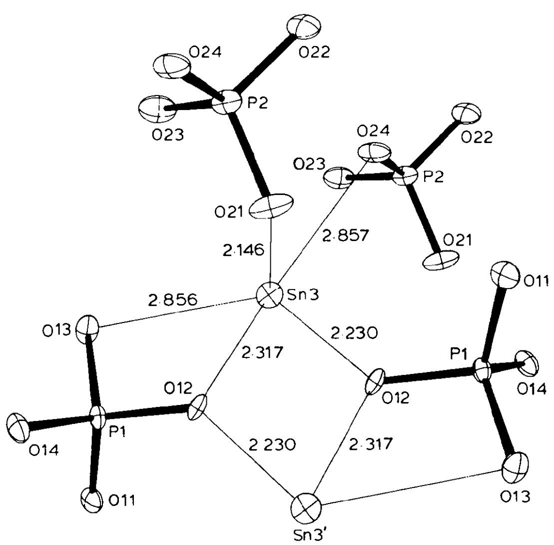

Fig. 3. The environment of Sn(3). The O(12)···O(12) edge of the trigonal pyramid is shared with Sn(3'), which is related to Sn(3) by a center of symmetry. Standard deviations for the distances given are 0·007 Å.

The geometry of the PO_4 groups in $Sn_3(PO_4)_2$ can be interpreted in terms of the ionic packing and the coordination of the O atoms. The P—O distances vary from 1·510 (7) to 1·544 (7) Å with a mean value of 1·535 Å, compared to 1·536 Å calculated for 64 orthophosphate groups (Baur, 1974). All O atoms except O(12) are strongly bonded to one Sn atom; O(12) forms two strong bonds *via* bridging. None of these primary contacts involve edge coordination of a PO_4 group. Each O atom except O(12) is also involved in a second weak Sn···O bond (Figs. 2 and 3). When weak Sn···O coordination is also taken into account, there are three PO_4 shared-edge coordinations, one for each Sn atom. In each case the associated O—P—O angle is significantly less than the ideal tetrahedral angle. The primary contact Sn(3)—O(12) at 2·317 Å and the secondary contact Sn(3)—O(13) at 2·856 Å result from edge coordination of $P(1)O_4$. The lengths of these contacts are more nearly equal than in the other cases of PO_4 edge coordination and the O(12)—P(1)—O(13) angle is the smallest. This shows that the extent of the PO_4 group distortions is also dependent on the secondary coordination of the O atoms.

The P—O—Sn angles for the primary coordinations vary widely over the range 111–141° (see Table 2) with a mean value of 128·5°. The four P—O—Sn angles in the range 111–122° might be taken as indicating a tendency toward sp^2 hybridization at the O atom. However, there are also four P—O—Sn angles in the narrower range 135–141°. Values in the neighborhood of 120° would also be expected from the repulsion of the P and two Sn atoms coordinated to the O. The wide variation of the P—O—Sn angles suggests that maintaining a strict bond direction at the O atom is not an important factor in determining the ionic arrangements in $Sn_3(PO_4)_3$.

We thank P. B. Kingsbury and B. Frana for technical assistance. The figures were drawn with an in-house augmented version of *ORTEP*, written by C. K. Johnson of Oak Ridge National Laboratory, Oak Ridge, Tennessee. This work was supported by Research Grant DE00572 to the American Dental Association Health Foundation, Research Grant DE04192 to Cornell College and NIDR Special Fellowship DE53209 to T. H. Jordan. All of the grants are from the National Institute of Dental Research (NIDR).

References

BAUR, W. H. (1974). *Acta Cryst.* **B30**, 1195–1215.
BERNDT, A. F. (1972). *J. Dent. Res.* **51**, 53–57.
COLLINS, R. (1962). PhD Thesis, Indiana Univ., Bloomington, Indiana.
COLLINS, R., NEBERGAL, W. & LANGER, H. (1961). *J. Amer. Chem. Soc.* **83**, 3724–3725.
DAVIES, C. G., DONALDSON, J. D., LAUGHLIN, D. R., HOWIE, R. A. & BEDDOES, R. (1975). *J. Chem. Soc. Dalton*, pp. 2241–2244.
DONALDSON, J. D. & PUXLEY, D. C. (1972). *Acta Cryst.* **B28**, 864–867.
FINGER, L. W. & PRINCE, E. (1975). *A System of Fortran IV Computer Programs for Crystal Structure Computations*, Nat. Bur. Stand. (US) Tech. Note 854.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
JORDAN, T. H., GERRITY, D. & HANUSA, T. (1976). Private communication.
JORDAN, T. H., SCHROEDER, L. W., DICKENS, B. & BROWN, W. E. (1976). *Inorg. Chem.* **15**, 1810–1814.
KAY, M. I., YOUNG, R. A. & POSNER, A. S. (1964). *Nature, Lond.* **204**, 1050–1052.
KLEMENT, R. & HASELBECK, H. (1963). *Chem. Ber.* **96**, 1022–1026.
LENHERT, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.
MCDONALD, R. C., HAU, H. H. & ERIKS, K. (1976). *Inorg. Chem.* **15**, 762–765.
MCDONALD, R. R., LARSON, A. C. & CROMER, D. T. (1964). *Acta Cryst.* **17**, 1104–1108.
SCHROEDER, L. W., PRINCE, E. & DICKENS, B. (1975). *Acta Cryst.* **B31**, 9–12.

Acta Cryst. (1977). **B33**, 1816–1820

The Structure of the Crystalline Complex of Purine and Urea (2:1)

BY AKIKO ITAI, HIROSHI YAMADA, TOSHIHIKO OKAMOTO AND YOICHI IITAKA
Faculty of Pharmaceutical Sciences, University of Tokyo, Tokyo, Japan

(*Received* 7 *October* 1976; *accepted* 17 *November* 1976)

$C_5H_4N_4.\frac{1}{2}(CH_4N_2O)$, FW 150·14, is orthorhombic, space group *Fdd*2, a = 20·921 (4), b = 35·274 (5), c = 3·622 (1) Å, V = 2672·9 Å^3, Z = 16, D_m = 1·490, D_x = 1·496 g cm^{-3}. The purine molecules are stacked along the c axis and are held together by N(9)–H···N(1) and N(urea)–H···N(7) hydrogen bonds. The protonation site in the imidazole ring is N(9) instead of the usual N(7) in purine. The overlapping mode of the purine molecules differs from that in the crystal of purine. The urea molecules are also associated with each other through hydrogen bonding. Two half-weight urea molecules are arranged around the diad axis parallel to [001] with their O atoms on the diad and their molecular planes nearly parallel to (010). Because of the short axial length of c, the repeat distance of the urea molecules must be a multiple of c, thus indicating disorder along the c axis.

Introduction

We found that purine and urea form a stable 2:1 molecular complex in the solid state. The complex retains the same stoichiometric ratio through sublimation at 105 °C/23 mmHg as well as recrystallization from various organic solvents. The infrared spectrum (in KBr) of the complex shows a drastic change in the 1550 ~ 1700 cm^{-1} region compared with the mixture of the same composition. At present, there is no evidence of the analogous complex formation in solution. In order to clarify the state of association between purine and urea in this molecular complex, we have carried out the crystal structure analysis.

Experimental

Crystals of the complex were prepared by dissolving purine and urea in a 2:1 stoichiometric ratio in warm ethyl acetate and allowing the mixture to stand at room temperature. A crystal 0·3 × 0·1 × 0·45 mm was cut with a razor and used for the X-ray experiments. X-ray data were collected on a Philips PW 1100 automatic diffractometer using Cu $K\alpha$ radiation monochromated by a graphite plate. The systematic absences (Table 1) established the orthorhombic, face-centred space group *Fdd*2. The calculated density, assuming 16 structural units in a cell, accorded well with that measured in CCl_4–n-hexane by flotation. This indicates that the urea