

Table 5. Comparison of structural parameters of the dithiodiketopiperazin moiety as found in sporidesmin, gliotoxin and chaetocin

	Sporidesmin*	Gliotoxin†	Chaetocin
C-C(keto)	1.52 Å	1.51 Å	1.53 Å
C(keto)-N	1.37	1.35	1.35
N-C	1.43	1.45	1.45
C=O	1.23	1.23	1.23
C-S	1.90	1.89	1.88
S-S	2.08	2.08	2.077
C-C(keto)-N	113°	114°	113°
C=C(keto)-N	124	125	125
C-C(keto)=O	124	122	123
C(keto)-N-C	114	118	118
N-C-C(keto)	112	111	111
C(keto)-C-S	102	103	103
N-C-S	112	111	112
C(keto)-C-S	102	103	103
N-C-S	112	111	112
C-S-S	98	98	98
C-S-S-C	-10	-12	+11

* Fridrichsons & Mathieson (1965).

† Fridrichsons & Mathieson (1967).

contacts. The shortest distances found are H...H=2.2 (2), S...H=3.0 (1), C...N=3.30 (1), S...C=3.41 (1) Å.

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The Crystal Structure of Silver Diethyl Phosphate, AgPO₂(OC₂H₅)₂

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The crystal structure of silver diethyl phosphate, AgPO₂(OC₂H₅)₂, was determined with 853 diffractometer-collected intensities. The space group is orthorhombic, *Pccn*, and the unit cell contains two formula units. The unit-cell dimensions at 23°C are $a=20.19$ (1), $b=14.35$ (4) and $c=5.86$ (1) Å. The intensities were measured by the 2θ -scan method with Mo $K\alpha$ radiation and the structure was solved by Patterson methods and refined by block-diagonal least-squares calculations to an R value of 0.043. The silver ion is coordinated to four oxygen atoms in a distorted tetrahedral arrangement with a mean Ag-O distance of 2.36 Å. Thermal motion of the atoms in the diethyl phosphate anion is high and can be qualitatively explained as a rigid-body motion of the phosphate group coupled with a librational motion of the ester groups about the P-O bonds. The ester conformation with respect to the phosphate group is *syn-clinal*, *anti-clinal*.

Introduction

A study of the conformation of diester phosphates is of interest both for the light it might throw on bonding within the phosphate group (Collin, 1966, 1969) and for its implications to the structure of nucleic acids (Sundaralingam, 1969) and other molecules of biological interest.

Although the structures of a number of phosphate diesters have been determined, that of barium diethyl

phosphate (Kyogoku & Iitaka, 1966) is the only acyclic ester in which the ester groups contain no ionic species, or species capable of hydrogen-bond formation.

Many silver salts exhibit short silver-oxygen distances in which partial covalent character may occur, and it is of interest to examine the effects of such interactions on the bonding scheme within the diester anion and on the resulting conformation. We suspect that conformational differences such as those between the

diethyl phosphate anion in the barium and silver salt, may be eventually correlated with cation–oxygen interactions.

Experimental

Crystal data

$\text{AgPO}_2(\text{OC}_2\text{H}_5)_2$, M.W. 260.96, Space group: *Pccn*
 $a = 20.19$ (1), $b = 14.35$ (4), $c = 5.86$ (1) Å
 $V = 1695.1$ Å³, $D_m = 1.997$ g.cm⁻³ (floatation),
 $D_c = 1.952$ g.cm⁻³

$Z = 8$

$F(000) = 1016$, Mo $K\alpha$ ($\lambda = 0.70926$ Å for $K\alpha_1$)

$\mu = 24.4$ cm⁻¹

Silver diethyl phosphate was prepared by adding excess silver oxide to diethyl chlorophosphate in aqueous solution. The mixture was stirred for five hours at room temperature. The precipitated silver chloride and unreacted silver oxide were filtered off and the solvent removed by vacuum distillation at room temperature.

The compound was recrystallized from 95% ethanol by addition of ethyl acetate, and analyzed for Ag (obs. 41.40%, calc. 41.33%), P (obs. 11.99%, calc. 11.87%), C (obs. 18.47%, calc. 18.41%) and H (obs. 3.91%, calc. 3.86%). The direct addition of ethyl acetate to the ethanol solution yields crystals which are no larger than 0.5 mm in two dimensions and up to several mm long. Single crystals of more suitable size and shape for the collection of diffractometer data were grown by allowing the ethyl acetate vapor to diffuse into an ethanol solution of silver diethyl phosphate. The crystal used in the experiment was a colorless rectangular prism with dimensions 0.15 × 0.13 × 0.25 mm which quickly darkened on standing.

The unit-cell dimensions were determined at 23°C from a least-squares fit of angular settings for ten reflections in the range $2\theta = 40$ – 45° where the α_1 – α_2 doublet is resolved. The systematic absences $0kl$ for l odd, $h0l$ for l odd and $hk0$ for $h+k$ odd, along with *mmm* reciprocal lattice symmetry, uniquely identify the space group as *Pccn*. The unit-cell dimensions and space group are in agreement with the results of Scanlon & Collin (1954).

Intensity data were collected on an automated Picker four-circle diffractometer with the c^* axis of the crystal offset approximately 2° from the ϕ axis of the instrument. Intensities were measured using the 2θ -scan method up to a maximum value of $2\theta = 50^\circ$ with Zr-filtered Mo $K\alpha$ radiation, a target take-off angle of 2.5° and a scan speed of 1° per min. The base width of the scan was 1.5° and the actual range of each scan was adjusted for increasing dispersion as 2θ increased.

The intensities of three standard reflections were remeasured every 60 reflections and used to correct the data for variations caused by drift in incident beam intensity or by slow crystal decomposition. A 5% decline in the standard intensities was observed between the start and finish of data collection. Values of $|F_o|$ were obtained from the intensity data by applying

corrections for the decline in the standard intensities and for the Lorentz and polarization factors. Within the angular range over which data collection was undertaken, there were 853 observed and 647 unobserved reflections by the criterion that a reflection was unobserved if its net count was less than 2.5 standard deviations above background. The intensities were corrected for absorption by an analytical method based on the actual shape of the crystal measured under a microscope.

Structure determination and refinement

The silver and phosphorus atom positions were determined from the highest peaks on a Patterson map. The resulting z coordinate of the silver atom was close to zero and that of the phosphorus atom was close to $\frac{1}{2}$. After two cycles of least-squares refinement on the position and isotropic thermal parameters of silver and phosphorus, the z coordinates of the two atoms had shifted somewhat, but were still close enough to their original positions so that the calculated magnitudes of structure factors with $h+k=2n+1$ were very small. As a result, the phases of most structure factors in this class were poorly determined at this stage. A three-dimensional Fourier synthesis was prepared, using as coefficients only those observed structure factors for which $|F_c| \geq 0.25|F_o|$ in an effort to limit the number of incorrectly phased reflections. If *all* reflections of the class $h+k=2n+1$ had been excluded from the Fourier synthesis, a false mirror plane would have been introduced at $z = \frac{1}{2}$. Because only a small number of reflections of this class were allowed to contribute to the first Fourier synthesis, vestiges of the false mirror remained. The electron density map yielded five peaks as possible oxygen atoms, two pairs of which were approximately mirror images, while a single peak appeared near $z = \frac{1}{2}$. The latter and a member of one pair, both with maximum densities of about $6 \text{ e.}\text{\AA}^{-3}$, were chosen as oxygen atoms O(1) and O(3) respectively. The other three peaks had densities of less than $4 \text{ e.}\text{\AA}^{-3}$. The position and isotropic thermal parameters of silver, phosphorus and the two newly located oxygen atoms were refined by three cycles of block-diagonal least-squares calculations. A second Fourier synthesis was prepared imposing the previous restrictions on the magnitudes of coefficients. The false mirror symmetry now vanished completely, and the two remaining oxygen atoms and one carbon atom, C(1), were located. Two more structure factor–Fourier map calculations with all observed reflections resulted in the location of all atoms except one carbon, C(3).

The shapes of the peaks in the electron density maps suggested that the carbon atoms and three of the oxygen atoms were undergoing large thermal motion. The structure at this stage was refined by three cycles of block-diagonal least-squares calculations on position and isotropic thermal parameters, and a set of F_c was obtained and used in a difference Fourier synthesis

Table 1. Observed and calculated structure factors $\times 10$

Unobserved reflections are indicated by an asterisk and the value of F_0 is replaced by the estimated threshold value.

Table with 16 columns (L, FO, FC, L, FO, FC, L, FU, FC, L, FU, FC, L, FO, FC, L, FU, FC) containing numerical data for various reflections. The table is organized into four groups of four columns each, representing different sets of reflections. Asterisks indicate unobserved reflections.

which yielded the position of the remaining carbon atom. Because of the large thermal motion of the ester carbon atoms, no attempt was made to locate hydrogen atoms. In this and subsequent least-squares calculations, the quantity minimized was $\sum w|F_o - F_c|^2$.

The position and anisotropic thermal parameters were refined by successive cycles of block-diagonal least-squares calculations with a weighting scheme $w = \{1 + [(|F_o| - 40)/50]^4\}^{-1}$ until all parameter shifts were less than 0.25 times the standard deviation of the parameter. After this refinement, the *R* index ($R = \sum |F_o - F_c| / \sum |F_o|$) based on observed reflections only was 0.043. The mean value of the final $w(|F_o| - |F_c|)^2$ showed little variation over the range of $|F_o|$. In all structure factor calculations, the atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1952) and corrections for anomalous dispersion by silver and phosphorus were made using the values given by Cromer & Liberman (1970). The observed and calculated structure factors are listed in Table 1. The final atomic positions are listed in Table 2 and the final thermal parameters are listed in Table 3.

Table 2. Fractional coordinates and estimated standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>
Ag	0.19051 (4)	0.17558 (5)	-0.01017 (11)
P	0.14186 (12)	0.09508 (18)	0.48733 (37)
O(1)	0.1600 (5)	-0.0084 (5)	0.4458 (16)
O(2)	0.0780 (4)	0.1067 (8)	0.3438 (16)
O(3)	0.1917 (3)	0.1589 (4)	0.3806 (9)
O(4)	0.1297 (4)	0.1061 (7)	0.7312 (11)
C(1)	0.1809 (8)	-0.0426 (9)	0.2412 (26)
C(2)	0.1734 (9)	-0.1458 (10)	0.2377 (38)
C(3)	0.0237 (10)	0.1280 (21)	0.3398 (45)
C(4)	-0.0262 (8)	0.1302 (14)	0.1860 (33)

Results and discussion

The overall structure is composed of independent columns, centered on the 2_1 axes parallel to *c*. Each column has four silver ions per repeat unit inside, close to the column axis, and four diethyl phosphate anions per repeat unit on the outside. Fig. 1 shows the packing of these columns within the unit cell.

A drawing of the diethyl phosphate anion in the

silver diethyl phosphate crystal is shown in Fig. 2. Table 3 shows that all atoms in the anion have moderate to large thermal motion (or disorder) which reaches a maximum r.m.s. radial displacement for C(3) of 0.95 Å. A marked apparent distortion of bond lengths and angles is expected to arise from such large thermal motion and, indeed, the C(4)-C(3) and C(3)-O(2) bonds of 1.35 and 1.14 Å are unreasonably short and the C(3)-O(2)-P angle of 147° is unreasonably large (Tables 4 and 5). A similar situation exists in the one other diethyl phosphate structure reported, barium diethyl phosphate (Kyogoku & Itaka, 1966), where thermal motion in the ester groups is high and a carbon-carbon bond length of 1.37 Å is reported. Corrections for thermal motion can only be made if a specific model for the relative motion of the various atoms is assumed. Such assumptions and their derived bond lengths are fraught with considerable uncertainty in this particular structure.

Table 4. Bond distances within the anion with thermal motion corrections

Estimated standard deviations are given in parentheses.

	Un-corrected	Rigid PO ₄	Corrected Lower limit	Upper limit
P—O(1)	1.549 (8) Å	1.57 Å	1.55 Å	1.78 Å
P—O(2)	1.548 (9)	1.58	1.57	1.87
P—O(3)	1.497 (6)	1.51	1.50	1.69
P—O(4)	1.459 (7)	1.49	1.47	1.80
C(1)—O(1)	1.363 (17)		1.36	1.77
C(3)—O(2)	1.138 (22)		1.18	2.12
C(2)—C(1)	1.488 (19)		1.48	2.01
C(4)—C(3)	1.353 (29)		1.37	2.26

Table 5. Bond angles within the anion

Estimated standard deviations are given in parentheses.

	Angle
O(1)—P—O(2)	102.4 (5)°
O(1)—P—O(3)	111.1 (4)
O(1)—P—O(4)	107.4 (5)
O(2)—P—O(3)	105.4 (4)
O(2)—P—O(4)	112.4 (5)
O(3)—P—O(4)	117.2 (4)
C(1)—O(1)—P	124 (1)
C(3)—O(2)—P	147 (2)
C(2)—C(1)—O(1)	110 (1)
C(4)—C(3)—O(2)	137 (2)

Table 3. Thermal parameters and their estimated standard deviations ($\times 10^4$)

Temperature factor = $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	R.m.s. radial displacement (Å)
Ag	0.0953 (4)	0.0899 (4)	0.0577 (4)	-0.0026 (6)	0.0019 (4)	0.0077 (4)	0.493
P	0.079 (1)	0.088 (1)	0.045 (1)	-0.019 (2)	0.000 (1)	0.000 (1)	0.461
O(1)	0.150 (7)	0.084 (5)	0.140 (8)	-0.026 (7)	0.025 (6)	0.006 (5)	0.612
O(2)	0.088 (5)	0.254 (12)	0.127 (7)	-0.028 (10)	-0.031 (6)	-0.021 (8)	0.686
O(3)	0.073 (4)	0.075 (4)	0.049 (3)	-0.012 (5)	0.004 (3)	0.000 (3)	0.444
O(4)	0.148 (7)	0.189 (9)	0.059 (4)	-0.091 (10)	0.012 (5)	-0.014 (5)	0.630
C(1)	0.192 (15)	0.084 (8)	0.140 (12)	-0.004 (13)	0.035 (12)	-0.028 (8)	0.645
C(2)	0.194 (17)	0.091 (9)	0.250 (23)	-0.012 (15)	-0.023 (17)	-0.014 (17)	0.731
C(3)	0.144 (16)	0.499 (40)	0.257 (25)	0.134 (31)	-0.104 (18)	-0.112 (30)	0.950
C(4)	0.123 (12)	0.241 (20)	0.181 (16)	0.001 (19)	-0.046 (12)	-0.051 (16)	0.739

An examination of the thermal ellipsoids in Fig. 2 and the r.m.s. radial thermal displacements in Table 3 rules out a rigid body motion of the whole molecule. The relatively small r.m.s. displacement of O(3) and the magnitudes and directions of the displacements of phosphorus and the other three oxygen atoms suggest that the PO_4 group itself may behave approximately as a rigid body with a major axis of rotation along the P–O(3) bond. The r.m.s. displacement of carbon atom C(3) is larger than that of the terminal carbon atom C(4) and this suggests the possibility of an additional librational motion of the ester group about the P–O bond.

An attempt to analyze the rigid body motion quantitatively was made with the computer program *MGTL* written by Schomaker & Trueblood (1968). It was impossible to obtain a satisfactory rigid body description in terms of all the heavy atoms of the anion, and this is in accord with the qualitative picture discussed above. With the PO_4 group alone as a rigid body an r.m.s.

value of 0.0059 \AA was obtained for the difference between the U_{ij} 's observed for the atoms in the PO_4 group and those calculated for rigid body motion. The model derived from these calculations has two main axes of librational motion. The first axis, associated with an r.m.s. amplitude of 13.2° , passes close to the phosphorus atom and makes an angle of 18.4° with the P–O(3) bond direction. The second axis, r.m.s. amplitude of 11.3° , is almost perpendicular to the first, but its intersection with it is displaced from the phosphorus atom by 0.80 \AA in the direction of O(3). The third principal axis is associated with a small negative value for the mean square amplitude of libration. Phosphorus–oxygen bond distances corrected for the rigid body motion of the PO_4 group are given in Table 4. The corrected bond lengths are in accord with those found for bonds from phosphorus atoms to esterified and non-esterified oxygen atoms (Karle & Britts, 1966; Kyogoku & Iitaka, 1966; Li & Caughlan, 1965).

The carbon–oxygen and carbon–carbon bond

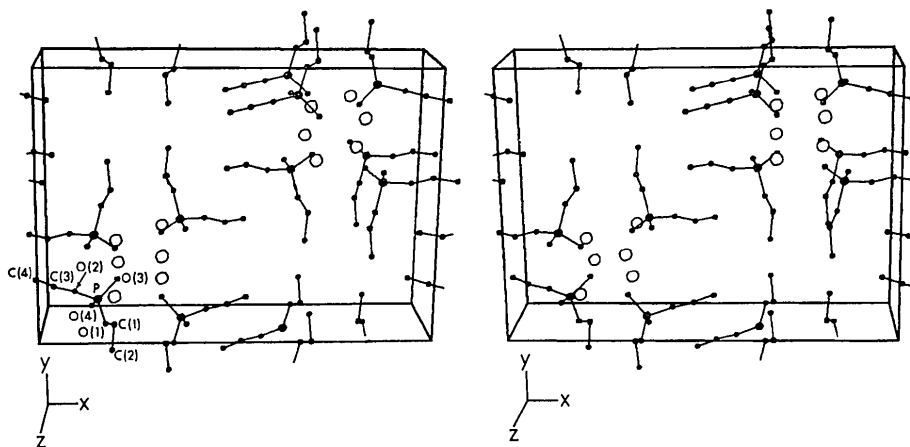


Fig. 1. A stereoscopic view of the unit-cell contents, looking down the column axes. Silver ions are indicated by the large open circles.

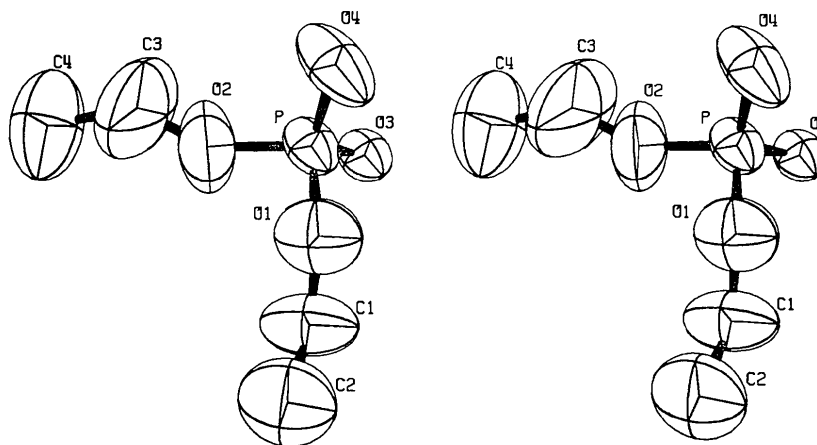


Fig. 2. A stereoscopic view of the diethyl phosphate anion.

lengths are all smaller than would be expected and this is undoubtedly connected with the large thermal motion of these atoms. The bond lengths and angles involving C(3) are quite unreasonable, but the upper and lower limits of the corrected bond lengths (Table 4) calculated by the method of Busing & Levy (1964), span a range that includes the commonly accepted values. Both the C(3)-O(2)-P and C(4)-C(3)-O(2) angles are considerably larger than what would be expected (120 and 110° respectively) but an apparent opening out of the C(3)-O(2)-P would be anticipated if considerable rotational motion of C(3) about the O(2)-P bond occurred. If, as is likely, the C(4) atom was constrained by intermolecular forces so that it could not take on large excursions, librational motion of C(3) about O(2)-P would be expected to open up the apparent C(4)-C(3)-O(2) angle.

This thermal-motion analysis and the bond-length corrections derived from it are consistent with a model for the diethyl phosphate anion which involves rigid-body motion of the PO₄ group, plus a rotational motion of each ester group about the P-O bonds. However, these two types of motion are correlated in such a manner as to prevent very large excursions of the terminal methyl groups. It is unlikely that any more stringent tests of the model can be applied to the U_{ij} 's because with the very large thermal motion present in the structure, the validity of fitting the motion with six U_{ij} 's is in itself questionable.

The silver ions are coordinated to four oxygen atoms in a distorted tetrahedral arrangement as shown in Fig. 3. Atom O(3) and atom O(4) are members of phosphate tetrahedra displaced one unit cell from each other along *c*. The Ag-O coordination distances and the O-Ag-O angles are listed in Table 6. The next closest Ag-O approach beyond the distorted tetrahedral coordination is at 3.64 Å.

Table 6. *Coordination distances and angles within the coordination tetrahedron of silver*

Estimated standard deviations are given in parentheses.

	Uncor- rected	Cor- rected*		
Ag-O(3)	2.303 (5) Å	2.376 Å	O(3)-Ag-O(4')	130.4 (3)°
Ag-O(3')	2.474 (6)	2.530	O(3)-Ag-O(3')	103.7 (2)
Ag-O(3'')	2.460 (6)	2.517	O(3)-Ag-O(3'')	111.1 (2)
Ag-O(4')	2.191 (8)	2.303	O(3')-Ag-O(4')	108.4 (3)
			O(3')-Ag-O(3')	90.9 (2)
			O(3'')-Ag-O(4')	105.3 (3)

* Corrected for thermal motion assuming no correlation between the motions of the silver and oxygen atoms.

The Ag-O distances within the coordination sphere of silver average 2.36 Å with two approaches of 2.19 and 2.30 Å which are much shorter than the other two. Short approaches of 2.34 Å in Ag₃PO₄ (Helmholtz, 1936) and 2.40 Å in AgCN 2AgNO₃ (Britton & Dunitz, 1965) have been attributed to partial Ag-O

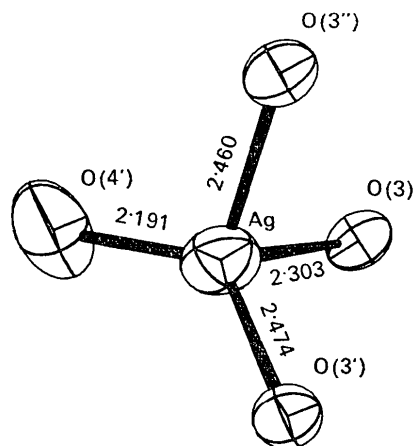


Fig. 3. Bond distances in the coordination sphere of the silver ion. O(4') is related to O(4) by $x, y, z-1$. O(3') is related to O(3) by $\frac{1}{2}-x, y, z-\frac{1}{2}$ and O(3'') is related to O(3) by $x, \frac{1}{2}-y, z-\frac{1}{2}$.

covalent bonding and it is likely that covalent interactions also exist in silver diethyl phosphate. However, in this case, effects of such partial covalent bonding on the phosphorus-oxygen bond lengths would be masked by the large thermal motion of the phosphate group.

The conformation of the ester groups with respect to the phosphate group can be described by the dihedral angle between the COP and OPO planes. Using the convention of Klyne & Prelog (1960) and the nomenclature of Sundaralingam (1969), these angles are $\omega=68^\circ$ for C(1)-O(1)-P-O(2) and $\omega'=125^\circ$ for C(3)-O(2)-P-O(1) and the conformation can be described as *syn-clinal* (sc), *anti-clinal* (ac). In barium diethyl phosphate (Kyogoku & Itaka, 1966), these angles are $\omega=68.2^\circ$ and $\omega'=71.6^\circ$ and the conformation is sc, sc.

Computer programs used

Fourier, least-squares and absorption calculations were carried out with the NRC crystallographic programs of Ahmed, Hall, Pippy & Saunderson (1966). The analyses of thermal motion were made with the ORFFE program of Busing, Martin & Levy (1964) and the program MGTL5 written by Schomaker & Trueblood (1968). The drawings were made with the ORTEP program of Johnson (1965).

The construction and programming of the computer-controlled diffractometer used in this work was partly supported by Biotechnology Resource Grant RR-220 from the National Institutes of Health. We are indebted to Dr David A. Goldstein of our department for the supervision of this effort and to Dr William R. Busing for supplying us with paper tapes of the programs used on the Oak Ridge computer-controlled diffractometer.

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Concerning Systems for the Generating and Coding of Layered, Tetrahedrally Close-Packed Structures of Intermetallic Compounds

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Planar, tetrahedrally close-packed structures containing pentagon-triangle primary nets are analyzed on the basis of their secondary-net tessellations and geometry. Included are: (1) the structures generated and coded by Pearson and Shoemaker containing secondary-net tessellations of 4^4 , 3^6 , $3^4 4^2$, and $3^2 4^3 4$; (2) the structures derived by Kripyakevich in which secondary-net tessellations of $3^4 4$ and $3^5 4$ occur; and (3) some structures, generated here for the first time, with some secondary-net tessellations of 3^5 . We have extended the coding scheme of Pearson and Shoemaker to describe the second group of structures. It becomes complicated for structures with secondary nets that are not based on two sets of parallel lines. However, the simpler code proposed by Kripyakevich does not uniquely define these structures. Neither coding scheme adequately describes the third group of structures.

Introduction

'Tetrahedrally close-packed' (t.c.p.) structures are structures in which all atoms have interpenetrating triangulated coordination polyhedra with coordination numbers (C.N.) 12, 14, 15 or 16, and in which all interstices are tetrahedral. Many of the known examples of t.c.p. structures are 'planar'; that is, they are generated by the alternate stacking of main (primary) layers, in mirror planes, consisting of hexagon- and/or pentagon-triangle nets of atoms and subsidiary (secondary) layers which are less dense and consist of triangle, rectangle-triangle, or rectangle nets between the mirror planes. The pentagons and the hexagons of the primary nets are covered antisymmetrically by the pentagons and hexagons of the neighboring primary nets, and the atoms of the interleaving secondary nets center (in projection) all the pentagons and hexagons of the primary nets.

In Fig. 1, projections are shown of fragments of structures which have primary nets consisting in (a) of

hexagons and triangles and in (b) of pentagons and triangles. The secondary nets in these two cases differ in geometry. They consist in (a) of (approximate) squares and (approximately) equilateral triangles, and in (b) of rectangles (ratio of the two sides about $\sqrt{3}/2$) and of isosceles triangles with two angles of about 55° and one angle of about 70° (Shoemaker & Shoemaker, 1969). The polyhedra surrounding the atoms of the secondary nets in (a) share triangular faces perpendicular to all edges of the squares and triangles in the secondary net, and in (b) share triangular faces perpendicular to the *short* edges of the triangles and rectangles, but share edges in the planes perpendicular to the *long* edges of the net. To emphasize this asymmetry in the secondary nets of pentagon structures we will indicate the long edges of the nets by full double lines and the short edges by full lines. (These lines connect second-nearest neighbors and do not represent bonded contacts.)

In analyzing possible t.c.p. structures it is convenient to consider the possible configurations of the secondary