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The Crystal Structure of Hopeite, $Zn_3(PO_4)_2.4H_2O$

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The structure of hopeite, $Zn_3(PO_4)_2.4H_2O$, has been redetermined. It crystallizes in the orthorhombic system with cell dimensions $a = 10.629$ (2), $b = 18.339$ (3), $c = 5.040$ (1) Å. The space group is *Pnma* and there are four molecules in the unit cell. Least-squares refinement has been completed on three-dimensional data (1471 structure factors). The H atoms have been located and included in the refinement with an isotropic temperature factor of 4.0. The final residual is 6.8%. The structure consists of $ZnO_2(H_2O)_4$ octahedra, ZnO_4 tetrahedra and PO_4 tetrahedra, none of which are regular; these polyhedra share corners and edges. The mean (uncorrected) bond lengths are 2.099 (3) Å in the $ZnO_2(H_2O)_4$ octahedron, 1.963 (3) Å in the ZnO_4 tetrahedron and 1.537 (3) Å in the PO_4 tetrahedron. The thermal vibrations have been analysed and the mean corrected bond length in the $ZnO_2(H_2O)_4$ octahedron is 2.101 Å, assuming riding motion.

Introduction

The crystal structure of hopeite has been determined twice with different results. In one case the structure reported (Mamedov, Gamidov & Belov, 1961; Gamidov, Golovachev, Mamedov & Belov, 1963) suggests that hopeite is similar to the diaspore AlOOH–goethite FeOOH structure and the structure factor of the (*hk*0) projection refined to a residual of 24% even without corrections for temperature factors. However, using the same projection, Liebau (1965) reported a completely different structure with certain similarities to the already reported structure of phosphophyllite, $Zn_2Fe(PO_4)_2.4H_2O$ (Kleber, Liebau & Piatkowiak, 1961); in this case a final residual of 14.4% was given.

In view of the completely different structure, it was decided to redetermine the structure with three-dimensional data.

Experimental

Attempts to grow crystals suitable for investigation failed but finally a naturally occurring specimen was obtained by courtesy of the Keeper of Minerals, Department of Mineralogy, British Museum (Natural History). The original source of the specimen was the Broken Hill Mines, North-Western Rhodesia (specimen number BM 1907, 240). The crystal chosen for the intensity measurements was colourless and of triangular prismatic habit parallel to [001]. The crystal optics and

Laue symmetry confirmed that the crystals belong to the orthorhombic system.

The cell dimensions were determined by a least-squares fit to 12 strong intensity diffraction beams on a four-circle diffractometer using monochromatic molybdenum radiation (Mo $K\alpha = 0.71070$ Å) and are $a = 10.629$ (2), $b = 18.339$ (3), $c = 5.040$ (1) Å. These values are in good agreement with values reported previously (Wolfe, 1940; Mamedov et al., 1961; Liebau, 1965).

The calculated density for $Z = 4$ is $D_x = 3.096 \pm 0.001$ g cm^{-3}; this is in good agreement with the value obtained by de Schulten (1904) on artificial crystals, 3.109 g cm^{-3}, and within the range of densities obtained by Spencer (1908), 3.0 to 3.1 g cm^{-3}, for natural crystals from the same area of Rhodesia as the present specimen.

Systematic absences ($hk0$ absent when $h = 2n + 1$, $0kl$ absent when $k + l = 2n + 1$, $h00$ absent when $h = 2n + 1$, $0k0$ absent when $k = 2n + 1$, $00l$ absent when $l = 2n + 1$) were obtained from the ($hk0$), ($hk1$) and ($hk2$) Weissenberg photographs and ($0kl$) and ($h0l$) precession photographs. These indicate the space group to be either $Pnma$ (No. 62) or $Pn2_1a$ (No. 33); the former was taken to be correct because of previous work (Gamidov et al., 1963; Liebau, 1965).

Integrated intensity data were collected on an automatic four-circle Stoe diffractometer using monochromatic molybdenum radiation. In this way the intensities of 1415 independent reflexions were measured; to these were added another 56 reflexions with zero intensity and all reflexions were processed. The intensity of a standard reflexion (0,13,1) was measured after every 25 reflexions.

The observed intensities were corrected for absorption (linear absorption coefficient = 77 cm^{-1}) and Lorentz–polarization factors.

Determination of the structure

The structure was solved, independently of previously reported structures, from a three-dimensional Patterson synthesis using 1276 reflexions of intensity greater than three times the appropriate standard deviation, and partially phased Fourier syntheses. The Fourier syntheses produced two sets of coordinates for the structure, designated S1 and S2.

These two structures are related to each other (Fig. 1) and the x and y coordinates in the second of these (S2) are in good agreement with those given by Gamidov et al. (1963). The projection is hence the same but

Table 1. Parameters and standard deviations after anisotropic refinement

The anisotropic temperature factor is defined as exp $\{-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl) \times 10^{-5}\}$.

|	x	y	z	B_{11} or B	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Zn(1)	0.23618 (13)	0.25000 (0)	0.57284 (29)	215 (10)	144 (4)	1151 (50)	0 (0)	42 (18)	0 (0)
Zn(2)	0.14267 (7)	−0.00087 (5)	0.20768 (16)	77 (6)	70 (2)	393 (29)	0 (3)	1 (10)	−15 (6)
P	0.10285 (16)	0.09421 (4)	0.72589 (35)	133 (12)	43 (4)	425 (56)	8 (6)	17 (21)	−19 (13)
O(1)	0.10737 (75)	0.25000 (0)	0.25730 (169)	214 (59)	190 (26)	760 (260)	0 (0)	−162 (109)	0 (0)
O(2)	0.38614 (73)	0.25000 (0)	0.84901 (183)	92 (55)	244 (30)	1550 (323)	0 (0)	−191 (115)	0 (0)
O(3)	0.33521 (57)	0.16977 (35)	0.33917 (133)	295 (46)	143 (17)	1971 (243)	80 (24)	99 (91)	110 (55)
O(4)	0.14010 (56)	0.17265 (30)	0.78465 (114)	413 (48)	80 (14)	993 (200)	−51 (22)	318 (83)	−68 (44)
O(5)	0.10004 (69)	0.07994 (33)	0.42983 (108)	822 (69)	106 (16)	268 (175)	132 (28)	−230 (91)	−59 (45)
O(6)	0.47552 (46)	0.07867 (29)	0.64140 (123)	54 (34)	78 (14)	2113 (228)	−17 (18)	−91 (76)	123 (48)
O(7)	0.19796 (45)	0.04067 (28)	0.86067 (103)	98 (34)	88 (14)	724 (173)	41 (18)	186 (66)	71 (41)
H(14)	0.122 (21)	0.188 (12)	0.121 (46)	4.0					
H(24)	0.456 (21)	0.198 (11)	0.792 (48)	4.0					
H(35)	0.233 (21)	0.134 (12)	0.248 (50)	4.0					
H(36)	0.396 (21)	0.136 (12)	0.493 (48)	4.0					

1Å

(a) (b) (c)
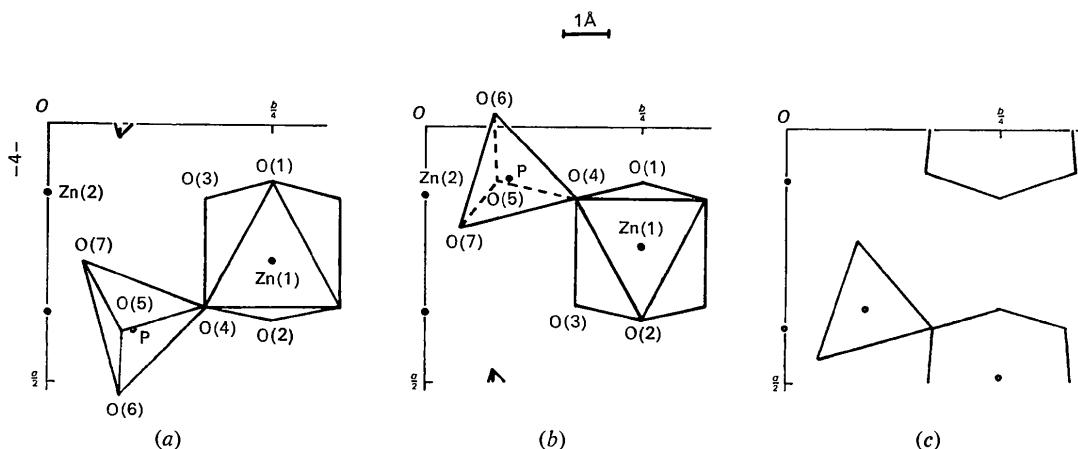
Fig. 1. The c-axis projections of three proposed structures of hopeite, (a) that designated S1, (b) that designated S2 and (c) that proposed by Liebau (1965).

their z coordinates obtained from packing considerations, are not the same. Fig. 1(c) is the (001) projection of the structure given by Liebau (1965). Again there are similarities between this structure and the other two, the main difference being a movement in the position of the atoms with respect to the origin. Incidentally there is a mistake in Liebau's Fig. 1; to agree with his coordinates the origin of this figure should be at the top left-hand corner instead of the bottom left-hand corner; this also transposes the diagram into a right-hand set of axes.

Each of these sets of coordinates received four cycles of least-squares refinement using individual isotropic temperature factors, and a weighting scheme such that $\omega = 1/\sigma^2$ (where σ is the standard deviation); the residuals of the initial data (R_0) and after each cycle of refinement $(R_1 - R_4)$ were as follows:

	R_0	R_1	R_2	R_3	R_4
S1	233·7%	64·5%	209·8%	93·0%	58·5%
S2	47·2	13·7	10·3	10·0	10·0

In addition, from the second cycle on, the output for the first crystal structure recommended negative temperature factors for all atoms except O(7). Because of this and the increased value of the residual the refinement of this structure was discontinued. The atomic scattering factors used for Zn, P, O and later H were those for the neutral atoms (*International Tables for X-ray Crystallography*, 1962).

At this stage in the investigation it was noticed that repeated measurements of the intensity of the standard reflexion varied by about $\pm 4\%$ and because of this the weighting scheme was altered so that $\omega = 1/(\sigma + 0.025 F_o)^2$ where F_o is the observed structure factor. The structure was then refined by full-matrix least-squares calculations, the function minimized being $\sum \omega \Delta F^2$; $\Delta F = F_{obs} - F_{calc}$. The refinement was continued for both isotropic and anisotropic temperature factors until the recommended shifts were less than one-tenth of the appropriate standard deviation (Mason, 1964).

Anisotropic refinement was completed and gave a final residual of 6·8% including zero intensities and 6·4% omitting them.

A three-dimensional difference Fourier synthesis using all data was calculated at the end of this refinement, but it was not possible to obtain the H positions from this owing to the large number of spurious peaks. However, the H atoms were obtained from a three-dimensional difference synthesis using only those reflexions for which $\sin \theta/\lambda \leq 1.1$ (616 reflexions). H(14), H(35) and H(36) were clearly visible but the fourth H could be either H(23) or H(24) and each of these positions was used in turn. With the same reflexions, the refinement was continued in stages as follows; first, only the heavy atoms were refined; secondly, the positions of the H atoms were refined alone, with a constant isotropic temperature factor of 4·0 for H and half the recommended shifts (H atoms are denoted by two numbers,
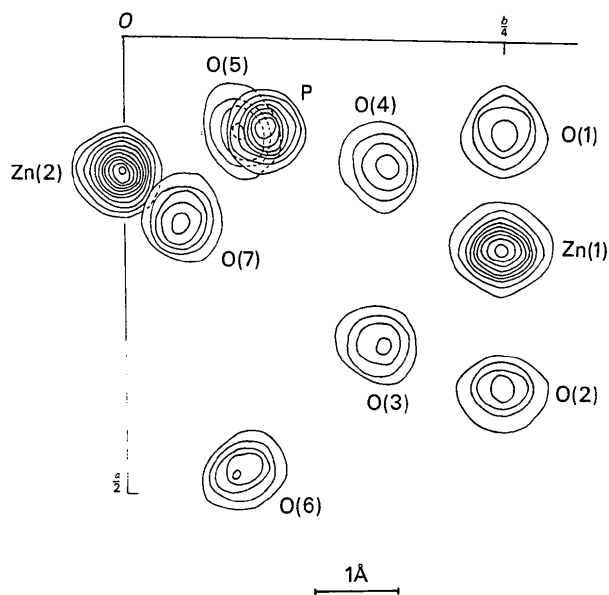

Fig. 2. A composite electron density map of the asymmetric unit calculated on sections through the atomic peaks. The contouring is at intervals of 12 e $Å^{-3}$ around the zinc, 8 e $Å^{-3}$ around the phosphorus and 4 e $Å^{-3}$ around the other atoms. The outermost contour is at the first interval.
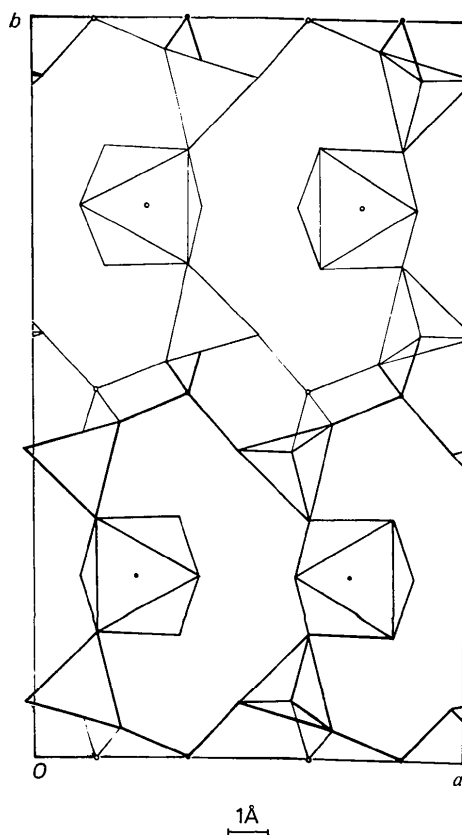

Fig. 3. The c-axis projection of the complete cell. Those groupings associated with zinc or phosphorus atoms with z coordinate equal to or greater than 0·5 are drawn with bold lines.

the first is that of the donor oxygen and the second that of the probable receptor oxygen).

The configuration involving H(23) could not be refined satisfactorily whereas that involving H(24) could, and so the latter was taken as the most probable position of the fourth H atom. Attempts to refine the temperature factors of the H atoms failed.

Still with the reduced set of data attempts were made to refine simultaneously the positions and temperature factors of the heavy atoms and the positions of the H atoms. This failed for H(24), so the attempt was repeated but this atom was excluded from the refinement. This latter refinement was successful and these coordinates of the H atoms are given in Table 1. It was noticed that the standard deviations of these coordinates increased by about 10% when attempts were made to simultaneously refine them with the heavy-atom coordinate and temperature factors. These increased standard deviations are included in Table 1, for H(24) as well as the others.

The positions and temperature factors of the heavy atoms were further refined by using the full data until the recommended shifts were again less than one tenth of the appropriate standard deviation (Mason, 1964). The final coordinates and temperature factors for all the atoms are given in Table 1; the final residual was 6·8% including zeros, 6·5% omitting them.

A composite electron density map of the asymmetric unit is given in Fig. 2.*

Discussion of the structure

The structure consists of ZnO_6 octahedra, ZnO_4 tetrahedra and PO_4 tetrahedra, all of which are significantly distorted (see below). The ZnO_6 octahedra consist of four H_2O molecules and two O atoms and thus may be represented as $ZnO_2(H_2O)_4$, the two O atoms in this polyhedron are shared with two PO_4 tetrahedra. Each PO_4 tetrahedron shares one corner with the ZnO_6 octahedron, two other corners with different ZnO_4 tetrahedra and an edge with a third. This means that one O atom, O(7), is involved in three polyhedra, one PO_4 and two ZnO_4 (this is discussed below). Each ZnO_4 tetrahedron shares two corners with two different PO_4 tetrahedra, an edge with a third and two corners with different ZnO_4 tetrahedra which are in identical positions in adjacent cells. A c-axis projection of the complete cell is given in Fig. 3, but to reduce possible confusion the ZnO_4 tetrahedron has not been shown as a tetrahedron but as four linkages to the appropriate O atoms.

Comparison of the present structure with that obtained by Liebau (1965) shows that the major differences are firstly that the atoms are all moved with respect to the origin and secondly that the orientation

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30961 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

of the phosphate tetrahedra with respect to the adjacent ZnO_6 octahedron is different. However the present structure is completely different from that of Mamedov et al., (1961). A further check on the possible error of the latter structure was obtained by using their coordinates as the initial data for four cycles of least-squares refinement. The residuals for the initial data and after four cycles of refinement using isotropic temperature factors were 62·0% and 58·6% respectively, thus indicating the essential incorrectness of their structure.

There would appear to be two major structural differences between hopeite and parahopeite (Kumbasar & Finney 1968; Chao, 1969). Both structures contain ZnO_6 octahedra where Zn is coordinated by four H_2O molecules and two O atoms. In hopeite the two O atoms are at adjacent corners of the octahedron while in parahopeite they are on opposite corners. Secondly both structures contain ZnO_4 tetrahedra but in hopeite each of these share two corners with others whereas in parahopeite they are independent.

Palache, Berman & Frondel (1963) mention that hopeite has three cleavages: {010} perfect, {100} good and {001} poor. Ignoring hydrogen bonds the first of these cleavages may be accounted for by the breaking of four Zn(1)–O bonds [two Zn(1)–O(3) and two Zn(1)–O(4)] per unit cell and the second by the breaking of four Zn(2)–O(6) bonds per unit cell. In view of the fact that the latter bonds are shorter than the former, this cleavage would be more difficult to accomplish and it would have to be stepped. The third cleavage requires the breaking of eight bonds per unit cell, four Zn(2)–O(7) and four Zn(2)–O(5) and would be even more difficult.

Bond lengths and angles uncorrected for thermal vibration

ZnO_6 octahedron

The individual values of the Zn–O and O–O distances are given in Table 2. The weighted mean values are: Zn–O 2·099 (3), O–O 2·955 (3) Å. Detailed examination of the individual values indicates that the octahedron is very distorted, the range of Zn–O distances being 12σ where σ is the largest individual standard deviation. In addition the O–Zn–O angles vary considerably over the range 84·5° to 94·0°, this range corresponding to 47σ. Some of this distortion may be due to thermal vibration but it is thought that, because equivalent values vary so much, the distortion must be due to additional causes.

Previous reported values of this bond length tend to be somewhat scattered (Table 3); the present value is in reasonable agreement with the others. Significant distortion ($> 3\sigma$) occurs in another compound in this table (Stählin & Oswald, 1970).

Of the four independent O atoms in this group, three will belong to H_2O molecules. Assuming that there is no hydrogen bonding between atoms within

the same octahedron and that the hydrogen bonds will be directed away from the Zn, then O(1), O(2) and O(3) will be H_2O molecules. This was confirmed by a difference synthesis. The position of the H atom associated with O(1) and O(3) was clearly obtained but that associated with O(2) could be either directed approximately towards O(3), designated H(23) or towards O(4^{ii}) designated H(24). The initial position of the former was obtained from the difference map as 0·3845, 0·1953, 0·9139 by Booth's (1948) method.

Consider now the sum of the angles $Zn-O-H_a$, $Zn-O-H_b$ and H_a-O-H_b. For O(1) and O(3) this is 333 (20)° and 317 (21)° respectively while for O(2) it is either 346 (25)° or 315 (21)° depending on whether the H atom is H(23) or H(24) respectively. The errors involved in these angles are so large that it is not possible to decide whether the water oxygen, the associated hydrogens and the zinc are coplanar.

If one considers the O atoms about each water O atom, then the sums of the angles subtended by these and the Zn atom are 309·8 (5)°, 288·0 (5)° for O(1) and O(3) respectively and 295·2 (5)° or 289·6 (5)° for O(2) depending on whether one considers O(3) or O(4^{ii}) to be the related atom. In either case it would appear that the atomic arrangement of the heavier atoms about the water oxygens is significantly not coplanar and this is different from the case of the $Mg.(H_2O)_6$ octahedron, where it is (Baur, 1964; Whitaker & Jeffery, 1970; Whitaker, 1973). Another point emerges: if the H atom associated with O(2) is H(23), could this be involved in a hydrogen bond to O(3)? As the configuration about O(3) is not significantly different from that about the

other atoms, it would appear that H(23), if it exists, does not take part in hydrogen bonding.

ZnO_4 tetrahedron

The individual values of the Zn–O and O–O distances are given in Table 2. The weighted mean values are: Zn–O 1·963 (3), O–O 3·189 (3) Å. Detailed examination of the individual values indicates that the tetrahedron is very distorted, the range of Zn–O distances being 14σ where σ is the largest individual standard deviation. In addition the angles vary over the range 103·2° to 121·3°, this range corresponding to 60σ.

Examination of previous recent results for this Zn–O distance (Table 3), shows that the mean values are in the range 1·947 (5) to 1·978 (5) Å. The present value is in excellent agreement with these. In addition significant distortion occurs in the ZnO_4 tetrahedron in several of these compounds (McDonald & Cruickshank, 1967; Chao, 1969; Baur & Tillmanns, 1970) and so the present results are in general agreement with previous ones.

Phosphate tetrahedron

The individual values of the P–O and O–O distances are given in Table 2. The weighted mean values are: P–O 1·537 (3), O–O 2·502 (3) Å. The mean value obtained for the P–O bond is in agreement with most of the results of other accurate investigations (Table 3). In this table not all the means and associated error have been given by the authors; some have been calculated from the individual results, in which case the weighted mean has been given.

Table 2. *Bond lengths and angles*

In this and subsequent tables, atoms in equivalent positions are represented by superscripts

(i)	$\bar{x}, \bar{y}, \bar{z};$			(iv)	$\bar{x}, \frac{1}{2}+y, \bar{z};$	(vi)	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$
(ii)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z;$			(v)	$x, \frac{1}{2}-y, z;$	(vii)	$\frac{1}{2}+x, y, \frac{1}{2}-z$
(iii)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z;$						

ZnO_6 octahedron

Zn(1)–O(1)	2·099 (8) Å	O(1)–O(3)	2·864 (9) Å	O(1)–Zn(1)–O(3)	84·5 (2)°
Zn(1)–O(2)	2·116 (9)	O(1)–O(4)	3·033 (9)	O(1)–Zn(1)–O(4)	94·0 (2)
Zn(1)–O(3)	2·159 (7)	O(2)–O(3)	3·010 (10)	O(2)–Zn(1)–O(3)	89·5 (2)
Zn(1)–O(4)	2·048 (6)	O(2)–O(4)	2·993 (9)	O(2)–Zn(1)–O(4)	91·9 (2)
Mean	2·099 (3)	O(3)–O(3^v)	2·943 (9)	O(3)–Zn(1)–O(3^v)	85·9 (2)
		O(3)–O(4)	3·057 (9)	O(4)–Zn(1)–O(4^v)	87·7 (2)
		O(4)–O(4^v)	2·837 (8)		
		Mean	2·955 (3)		

ZnO_4 tetrahedron

Zn(2)–O(5)	1·912 (6) Å	O(5)—O(6^{iv})	3·349 (8) Å	O(5)—Zn(2)–O(6^{iv})	121·3 (3)°
Zn(2)–O(6^{iv})	1·930 (5)	O(5)—O(7)	3·136 (8)	O(5)—Zn(2)–O(7)	106·7 (2)
Zn(2)–O(7)	1·997 (5)	O(5)—O(7^{iv})	3·102 (8)	O(5)—Zn(2)–O(7^{iv})	105·0 (3)
Zn(2)–O(7^{iv})	1·999 (5)	O(6^{iv})–O(7)	3·193 (7)	O(6^{iv})–Zn(2)–O(7)	108·8 (3)
Mean	1·963 (3)	O(6^{iv})–O(7^{iv})	3·227 (7)	O(6^{iv})–Zn(2)–O(7^{iv})	110·4 (2)
		O(7)—O(7^{iv})	3·131 (7)	O(7)—Zn(2)–O(7^{iv})	103·2 (2)
		Mean	3·189 (3)		

Phosphate tetrahedron

P–O(4)	1·521 (6) Å	O(4)–O(5)	2·504 (8) Å	O(4)–P–O(5)	111·1 (3)°
P–O(5)	1·515 (6)	O(4)–O(6)	2·484 (8)	O(4)–P–O(6)	108·7 (3)
P–O(6)	1·536 (5)	O(4)–O(7)	2·526 (8)	O(4)–P–O(7)	109·9 (3)
P–O(7)	1·564 (5)	O(5)–O(6)	2·534 (8)	O(5)–P–O(6)	112·3 (4)
Mean	1·537 (3)	O(5)–O(7)	2·513 (8)	O(5)–P–O(7)	109·4 (3)
		O(6)–O(7)	2·465 (7)	O(6)–P–O(7)	105·3 (3)
		Mean	2·502 (3)		

The only result significantly different from the present one is that from one of the phosphate groups in $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971). An examination of the individual bond lengths in this structure gives an average of 1·535 Å but the weighted mean (calculated by the present writer from the individual values) is 1·512 Å; this large difference is due to the better accuracy of the shorter bonds. However in this particular case the difference may be accentuated by rounding off the individual errors in the original paper to one significant figure which is either 1 or 2. As a result it is suggested that authors should either not round off errors to one significant figure or report a weighted mean calculated from data prior to rounding off.

Examination of the individual distances and angles in Table 2 indicates that the tetrahedron is distorted both in bond lengths and bond angles. In some cases the differences from the means are greater than three times the appropriate standard deviation. This is particularly so for O(7) for which the P–O bond length is large enough to suggest the possibility of a P–OH bond. However, on the assumption that the hydrogen bond would be directed away from the P, this would put the H atom near to Zn(2). Hence this distortion must be due to some other cause.

Table 3. *Comparison of observed bond lengths*

Reference	Compound	Zn–O
ZnO₆ octahedron		
Ansell & Katz (1966)	$Zn_2Mo_3O_8$	2·113 (5)
*Chao (1969)	$Zn_3(PO_4)_2.4H_2O$	2·108 (3)
Stählin & Oswald (1970)	$Zn_5(OH)_8(NO_3)_2.2H_2O$	2·135 (6)
		2·122 (6)
These results	$Zn_3(PO_4)_2.4H_2O$	2·099 (3)
ZnO₄ tetrahedron		
Ansell & Katz (1966)	$Zn_2Mo_3O_8$	1·978 (5)
McDonald & Cruickshank (1967)	$Zn_4Si_2O_7(OH)_2.H_2O$	1·955 (2)
*Chao (1969)	$Zn_3(PO_4)_2.4H_2O$	1·953 (3)
Stählin & Oswald (1970)	$Zn_5(OH)_8(NO_3)_2.2H_2O$	1·947 (6)
Baur & Tillmanns (1970)	$Zn_3(BO_3)_2$	1·968 (5)
		1·960 (5)
		1·968 (5)
These results	$Zn_3(PO_4)_2.4H_2O$	1·963 (3)

Reference	Compound	P–O
Phosphate tetrahedron		
Liminga (1965)	$N_2H_5H_2PO_4$	1·538 (2)
Liminga (1966)	$N_2H_6(H_2PO_4)_2$	1·537 (2)
Sutor (1967)	$MgHPO_4.3H_2O$	1·544 (2)
Araki & Zoltai (1968)	$Al_3(PO_4)_2(OH)_3$	1·526 (2)
Greenblatt, Banks & Post (1969)	Ca_2PO_4Cl	1·541 (1)
*Chao (1969)	$Zn_3(PO_4)_2.4H_2O$	1·545 (3)
Whitaker & Jeffery (1970)	$MgNH_4PO_4.6H_2O$	1·537 (1)
Tillmanns & Baur (1971)	$Na_3PO_4(NaOH)_{0-0.25}.12H_2O$	1·526 (2)
Dickens & Bowen (1971)	$Ca(H_2PO_4)_2.H_2O$	1·512 (1)
		1·535 (1)
Dickens, Bowen & Brown (1972)	$CaHPO_4$	1·5411 (5)
Mackie, Elliott & Young (1972)	$Ca_5(PO_4)Cl$	1·534 (1)
		1·534 (1)
		1·532 (1)
Khan, Roux & James (1972)	$(NH_4)_2HPO_4$	1·5395 (5)
Rea & Kostiner (1972a)	$Mn_2(PO_4)Cl$	1·542 (2)
Rea & Kostiner (1972b)	$Mn_2(PO_4)F$	1·537 (1)
Rea & Kostiner (1972c)	$Mg_2(PO_4)Cl$	1·538 (1)
Sudarsanan & Young (1972)	$Sr_5(PO_4)_3OH$	1·540 (2)
Sudarsanan, Young & Donnay (1973a, b)	$Cd_5(PO_4)_3Cl$	1·5395 (5)
Dickens, Brown, Kruger & Stewart (1973)	$Ca_4(PO_4)_2O$	1·533 (2)
		1·537 (2)
		1·536 (2)
		1·542 (2)
Dickens, Prince, Schroeder & Brown (1973)	$Ca(H_2PO_4)_2$	1·5409 (3)
		1·5407 (3)
Catti & Ferraris (1974)	NaH_2PO_4	1·5423 (5)
Ferraris & Franchini-Angela (1974)	$NaNH_4HPO_4.4H_2O$	1·541 (2)
Gatehouse & Miskin (1974)	$NaAl_3(PO_4)_2(OH)_4$	1·541 (2)
		1·540 (2)
Sudarsanan & Young (1974)	$Sr(PO_4)_3Cl$	1·540 (1)
These results	$Zn_3(PO_4)_2.4H_2O$	1·537 (3)

* Results for parahopeite.

Examination of the coordination about each O atom shows that for the three atoms O(4), O(5) and O(6), each is involved in the coordination polyhedron about one Zn whereas O(7) is involved in the coordination about two Zn atoms. In parahopeite (Chao, 1969) there is a similar state of affairs; again there is one O atom involved in coordination about two Zn atoms whereas the other three are coordinated to a single Zn, and again the first atom has a significantly longer P–O bond than the others.

Significant distortion of the orthophosphate tetrahedron that may be accounted for in the same manner also occurs in $Mn_2(PO_4)Cl$ (Rea & Kostiner, 1972a), $Mg_2(PO_4)Cl$ (Rea & Kostiner, 1972c) $NaAl_3(PO_4)_2(OH)_4$ (Gatehouse & Miskin, 1974).

The case of $Mn_2(PO_4)Cl$ (Rea & Kostiner, 1972a) is interesting in that one oxygen is involved in three coordination polyhedra while the other three oxygens are involved in two coordination polyhedra and the first oxygen is involved in a significantly longer P–O bond. However, in the chemically similar $Mn_2(PO_4)F$ (Rea & Kostiner, 1972b) all O atoms are involved in two coordination polyhedra and the linear distortion of the phosphate group is not significant.

A similar effect occurs in the orthoarsenates (Calvo & Leung, 1969) but the magnitude is much greater; Finney (1966) has found individual As–O bonds in the range 1·615 to 1·773 Å in $Cu_2(AsO_4)OH.3H_2O$. The greater effect is no doubt due to the As–O bond being longer and thus weaker than the P–O bond and because of this the effect of being involved in coordination to a cation is somewhat greater.

There are, of course, other causes of distortion in the orthophosphate tetrahedron. In the case of $Na_3PO_4(NaOH)_{0-0.25}.12H_2O$ it was found (Tillmanns & Baur, 1971) that if the O atoms of a phosphate group are receptor atoms of a hydrogen bond then this also lengthens the appropriate P–O bond. In the present case three of the four phosphate oxygens are receptor atoms for hydrogen bonds and these three are associated with the three shortest P–O bonds. Hence this effect is much smaller than that of being coordinated to an extra cation as the fourth oxygen, this one would expect from a consideration of the interatomic distances involved.

Consider the sum of the angles about each of the phosphate oxygens in turn; for O(7) the nearest neighbours are two Zn and a P atom, for O(5) and O(6) they are a Zn, a P and a donor O atom, while in addition to these O(4) may have a second donor. The sum of the

angles about O(5), O(6) and O(7) are 325·0 (6)°, 358·6 (5)° and 360·6 (5)° respectively while if we ignore the effect of the second donor atom this sum is 359·9 (5)° for O(4). In view of the fact that this is not significantly different from the others, it would appear that the hydrogen-bonding effect of H(24) is too weak to affect the configuration.

Hydrogen bonding

As already mentioned the H_2O molecules were confirmed by a difference synthesis. The positions of three H atoms H(14), H(35) and H(36) were clearly obtained but that associated with O(2) could be directed either approximately towards O(3), i.e. H(23) or towards O(4), i.e. H(24). In an attempt to decide which of these could be the fourth H atom the distances and angles involved in both schemes were calculated and so were those involving H(14), H(35), and H(36) for comparison (Table 4).

Regardless of whether H(23) or H(24) is considered to be correct, the distance and angles involving them are similar with one exception, $O_a–O_b$. By itself this might be taken as evidence that H(23) is the more probable as the value in this case, 2·926 (10) Å, lies well within the accepted range of hydrogen-bond lengths (Pimentel & McClellan, 1960), whereas the same interatomic distance for H(24), 3·123 (9) Å, is near the end of the range. This view is reinforced by the fact that the shortest non-bonded O–O distance is 3·077 Å and so if H(24) is present the bond must be weak or non-bonding.

On the other hand one would expect a receptor atom to be an oxygen rather than a water molecule as the negative charge on the former would be larger than the latter due to the effect of the hydrogens. This in turn would lead to a greater dipole in the bond.

However, previous discussion concluded that neither H(23) nor H(24) took part in hydrogen bonding and the most probable bonding is that shown schematically in Fig. 4. Thus the only evidence would appear to be computational in that H(24) partially refined whereas H(23) did not; however in this case we are left with the query as to why it did not refine fully as the other three hydrogens did. This raises another possibility: could the hydrogen be in positions H(23) and H(24) at random? The angles H(23)–O(2)–H(23^v) (143 ± 18°) and H(24)–O(2)–H(24^v) (100 ± 14°) are not significantly different from the tetrahedral angle and neither is H(23)–O(2)–H(24^v) (144 ± 16°), thus allowing com-

Table 4. *Distances (Å) and angles (°) involved in hydrogen bonding*

Donor O_a (water)	H	Receptor O_b	$O_a–O_b$	$O_a–H$	$H–O_b$	$O_b–O_a–O_b$	$H–O_a–H$	$O_a–H–O_b$
O(1)	H(14)	O(4)	2·794 (9)	1·33 (22)	1·73 (23)	61·0 (2)	116 (14)	131 (16)
O(2)	H(23)	O(3)	2·926 (10)	1·06 (21)	2·26 (24)	60·4 (3)	143 (18)	119 (16)
O(2)	H(24)	O(4)	3·123 (9)	1·24 (21)	2·05 (22)	54·0 (2)	100 (14)	142 (15)
O(3)	H(35)	O(5)	3·029 (9)	1·35 (23)	1·95 (23) ⎱	92·0 (2)	114 (15)	⎰ 132 (17)
O(3)	H(36)	O(6)	2·708 (8)	1·18 (23)	1·54 (23) ⎰			⎱ 166 (20)

plete randomness among the sites. In some ways this is the most satisfactory explanation as it accounts for both the appearance of the difference map and the difficulty in refining the atoms.

Although in the cases of the hydrogen bonds which are known to exist, the angles subtended by the hydrogen at the water oxygen are tetrahedral it is noticeable that in one case, O(1), the angle subtended by the receptor oxygens is considerably smaller. Although this effect has been obtained previously in oxalic acid dihydrate (Garrett, 1954), by neutron diffraction, the present angle is smaller than that found before. In the case of oxalic acid dihydrate it was found that the hydrogen bond was non-collinear so that the H atoms subtended an angle of 109° at the donor oxygen although the receptor atoms did not. This may be the case in hopeite but the errors in the angles associated with the hydrogen atoms are too large to confirm this.

Analysis of thermal vibrations

The r.m.s. displacements and the direction cosines of the thermal vibration ellipsoids are given in Table 5. The errors in the displacements were obtained by calculating the vibration ellipsoids for the values in Table 1 plus the standard deviations, and minus the standard deviations and averaging over similar atoms.

In the case of the ZnO_6 octahedron it can be seen that for Zn(1) and O(1) the vibration ellipsoids approximate to a prolate sphere with the unique axis of vibration parallel to the b axis while for O(3) the distortion from spherical symmetry is not significant and for O(4) the vibration ellipsoid again approximates to a prolate sphere. Considering these O atoms about
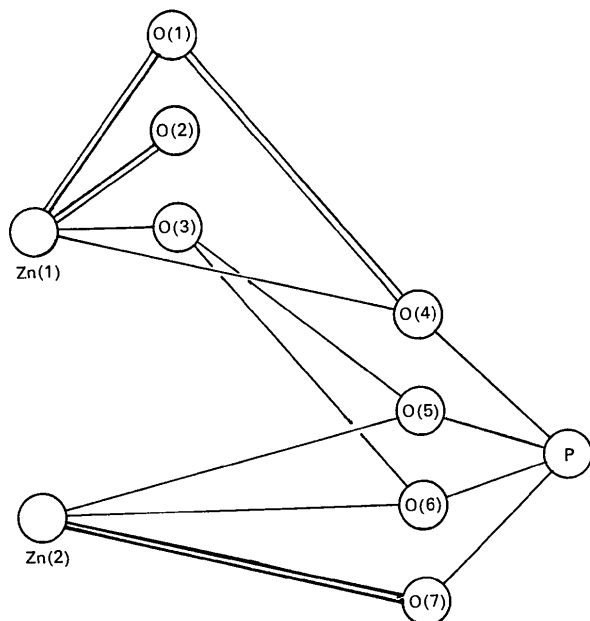

Fig. 4. Schematic diagram of proposed bonding.

Table 5. *R.m.s. displacements and orientation with respect to crystallographic axes*

	R.m.s. displacement	Direction cosine with respect to		
		a	b	c
Zn(1)	0·157 (2)	0·000	1·000	0·000
	0·122 (2)	0·212	0·000	0·977
	0·110 (2)	0·977	0·000	−0·212
Zn(2)	0·109 (2)	0·000	0·999	−0·051
	0·071 (2)	0·021	0·051	0·998
	0·066 (2)	0·999	−0·001	−0·021
P	0·088 (4)	0·807	0·589	−0·031
	0·085 (4)	0·573	−0·771	0·276
	0·073 (4)	−0·138	0·241	0·961
O(1)	0·180 (14)	0·000	−1·000	0·000
	0·116 (14)	0·863	0·000	−0·505
	0·092 (14)	−0·505	0·000	−0·863
O(2)	0·204 (14)	0·000	−1·000	0·000
	0·143 (14)	0·169	0·000	−0·986
	0·069 (14)	0·986	0·000	0·169
O(3)	0·169 (14)	−0·305	−0·683	−0·664
	0·151 (14)	−0·243	−0·618	0·748
	0·123 (14)	0·921	0·390	−0·023
O(4)	0·161 (14)	0·915	−0·232	0·331
	0·115 (14)	0·318	0·919	−0·235
	0·105 (14)	−0·249	0·320	0·914
O(5)	0·221 (14)	0·975	0·211	−0·074
	0·129 (14)	0·215	−0·975	0·051
	0·056 (14)	0·061	0·066	0·996
O(6)	0·167 (14)	−0·042	0·192	0·980
	0·113 (14)	−0·108	−0·977	0·187
	0·054 (14)	0·993	−0·098	0·062
O(7)	0·127 (14)	−0·252	−0·914	−0·317
	0·098 (14)	0·344	−0·390	0·854
	0·064 (14)	0·904	−0·106	−0·413

Zn(1) – O(1), O(2), O(3) and O(4) – the shortest axes of vibration make angles of 10°, 31°, 73° and 68° with the respective bond. In view of the shape of the vibration ellipsoids of O(3) and O(4), the errors in the last two angles are probably very large and probably what are more important are the directions of the largest axes. These make angles of 90°, 90°, 75° and 83° with the respective bond for O(1), O(2), O(3) and O(4).

Consider Zn(2); the vibration ellipsoid for this approximates to a prolate sphere with the unique axis parallel to the b axis. However, there would appear to be nothing special about the four oxygen neighbours, O(5), O(6^{iv}), O(7) and O(7^{iv}). Calculation of the orientations of the vibration ellipsoids of these four atoms indicates that the longest axes are at angles of 84°, 87°, 82° and 76° with respect to the respective bond while the shortest axes are at angles of 52°, 56°, 54° and 15° to the respective bonds for O(5), O(6^{iv}), O(7) and O(7^{iv}) respectively.

The vibration of the phosphorus atom is isotropic, while of its neighbours, only the vibration ellipsoid of O(4) would appear to be anything other than general; it approximates to a prolate sphere. In the case of the four oxygen neighbours, the longest axes of vibration of O(4), O(5), O(6) and O(7) are at angles of 48°, 89°, 70°, and 74° to the respective P–O bond, while the shortest ones are at angles of 65°, 7°, 30° and 62° respectively.

Bond lengths corrected for thermal vibrations

Busing & Levy (1964) have pointed out that one of the effects of thermal vibration is to alter the apparent bond lengths and they showed how to correct for the effect. Values of the bond lengths are included in Table 6, corrected for three of the cases they discuss; (A) the atoms are vibrating in phase, (B) the outer atoms are 'riding' on the inner ones and (C) the atoms are moving independently of each other.

Table 6. *Bond lengths corrected for thermal vibrations*

	Un-corrected bond length	Corrected bond length			
		A (in phase)	B (riding)	C (inde-pendent)	Standard deviation
Zn(1)–O(1)	2·099 Å	2·099 Å	2·101 Å	2·118 Å	0·008 Å
Zn(1)–O(2)	2·116	2·117	2·121	2·137	0·009
Zn(1)–O(3)	2·159	2·159	2·161	2·177	0·007
Zn(1)–O(4)	2·048	2·048	2·049	2·065	0·006
Mean	2·099	2·099	2·101	2·118	0·003
Zn(2)–O(5)	1·912	1·916	1·923	1·930	0·006
Zn(2)–O(6ⁱᵛ)	1·930	1·931	1·936	1·942	0·005
Zn(2)–O(7)	1·996	1·996	1·998	2·005	0·005
Zn(2)–O(7ⁱᵛ)	1·999	1·999	2·002	2·009	0·005
Mean	1·963	1·964	1·968	1·975	0·003
P–O(4)	1·521	1·523	1·529	1·538	0·006
P–O(5)	1·515	1·521	1·532	1·542	0·006
P–O(6)	1·536	1·538	1·544	1·552	0·005
P–O(7)	1·564	1·565	1·567	1·575	0·005
Mean	1·537	1·539	1·545	1·554	0·003

In the case of the oxygen octahedra about Zn(1) the longest r.m.s. displacements of the O atoms are almost perpendicular to the respective bonds while the displacement along the bond is much shorter. In addition this displacement is approximately the same as for Zn(1). This suggests that these O atoms are riding on the zinc; however O(4) is also bonded to phosphorus and so its vibration ellipsoid must be affected by both Zn(1) and P, suggesting that it may be vibrating with some independence of both. However, it would appear that, in general, the riding corrected value would be the best, thus Zn–O = 2·101 (3) Å when the zinc is octahedrally coordinated.

In the case of the water tetrahedron about Zn(2), the longest r.m.s. displacements of the O atoms are almost perpendicular to the respective bonds while the displacement along the bond is shorter. In addition the displacement is approximately the same as for the zinc and so the riding model would appear preferable. However, the picture is more complicated; all four O atoms are bonded to a P atom and one of them [O(7)] to another Zn(2) as well. Probably as a result of these other bonds, only for one atom [O(7ⁱᵛ)] is the shortest axis of vibration even approximately parallel to the respective Zn–O bond. Another way of examining this is to look at the phosphate tetrahedron. One O atom, O(4), is vibrating independently of the P atom and appears to be riding on Zn(1). For the other three

oxygens, however, their longest r.m.s. displacements are almost perpendicular to the respective bonds while the displacement along the bond is shorter. Again this displacement is approximately the same as for the phosphorus and so the riding model would again appear preferable. However these three O atoms cannot be riding simultaneously on Zn(2) and P and thus it would appear that oxygen atoms coordinated to both Zn(2) and P must, to a considerable extent, be vibrating independently of both. Consequently it is not possible to evaluate a corrected bond length for either the tetrahedral Zn–O or the P–O distance, but presumably the best values would be between those for the riding and independent models.

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The Crystal Structure and Molecular Conformation of Cyclo-L-prolyl-L-prolyl-L-hydroxyproline, a Cyclic Tripeptide

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The cyclization of three peptides to form a nine-membered ring introduces a certain amount of strain in the geometry of the peptide unit. This first crystal structure analysis of a cyclic tripeptide ($C_{15}H_{21}O_4N_3$) has shown that all three peptide units are in the *cis* conformation. The planarity of the peptide units is not unduly disturbed, but the three bonds involving the nitrogen atom are not coplanar. The three pyrrolidine rings are puckered differently, the atoms out of plane in the three cases being N, C^α and C^β respectively. The hydroxyl oxygen of the hypro group in this molecule is disordered, occupying two positions, both of which are able to participate in hydrogen bonding. The crystal belongs to the orthorhombic space group $P2_12_12_1$ with unit-cell parameters, $a=16\cdot284$, $b=9\cdot449$, $c=9\cdot260$ Å and $Z=4$. The structure was solved by direct methods with the *MULTAN* program and refined by full-matrix least-squares calculations to a reliability index of 6·2 %.

Introduction

In proteins and polypeptides, the building block is almost invariably the *trans* peptide unit. However there are situations where the *cis* peptide is incorporated in molecules for specific stereochemical reasons. A class of compounds containing *cis* peptides comprises the cyclic peptides having a small number of peptide units. In the diketopiperazines, the two *cis* peptides are cyclized to form a six-membered ring (Corey, 1938; Karle, 1972). It has been predicted that three peptides can be cyclized only if all three are in the *cis* conformation (Venkatachalam, 1968). As the number of peptide units increases, the *trans* peptide is increasingly preferred (Dale & Titlestad, 1970; Kopple, Onishi & Go,

1969; Kopple, 1971). Cyclo-L-Pro-L-Pro-L-Pro is the first cyclic tripeptide to be synthesized (Rothe, Steffan & Rothe, 1965). The derivatives of this compound were later synthesized and studied by n.m.r. spectroscopy by Blout and coworkers (Debar, Torchia & Blout, 1971). The structural parameters of cyclo-L-Pro-L-Pro-L-Pro were deduced from empirical calculations using stereochemical criteria (Venkatachalam, 1968). In these calculations it was shown that the three peptides have to be in the *cis* conformation for ring closure to occur. The two assumptions made in these calculations were: (1) the proline rings were planar and (2) the three bonds connected to the nitrogen atom were coplanar. To avoid short intramolecular contacts between the C^α protons, the torsion angle ω (a measure