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Dependence of the Distortion of the Tetrahedra in Acid Phosphate Groups H_nPO_4 ($n = 1$–3) on Hydrogen-Bond Length

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Abstract

The distortions of the PO_4 tetrahedra of acid phosphate groups H_nPO_4 ($n = 1$-3) have been studied by examining the correlations of the P-O bond lengths, OPO angles, O-O lengths and Baur's distortion indices with the hydrogen-bond length O-H···O. All three distortion indices correlate with O-H···O, indicating that the PO_4 distortion becomes larger with an increase in O-H···O. The individual or average P-O lengths, OPO angles and O-O lengths also correlate with O-H···O. This is most pronounced for P-O, least for O-O. The mean values of P-O, OPO and O-O are reasonably constant in each H_nPO_4 type, most notably in the case of OPO. The dependence of the PO_4 distortion on O-H···O can be described approximately by a model in which the P atom shifts away from the centroid of the regular tetrahedral framework, while retaining $3m$ site symmetry for HPO_4-type structures and $mm2$ symmetry for H_2PO_4-type structures.

Introduction

The bond lengths and angles of structural moieties in crystals, for example, tetrahedral XO_4-type ions and carboxyl groups, are known to deviate from regularity depending on the number and kinds of neighboring cations. For PO_4 groups the deviation from a regular tetrahedral arrangement has been extensively investigated by Baur (1974) for various kinds of PO_4 groups in crystals. He examined the P-O distances, O-P-O angles, O-O distances, their distortion indices and the bond strengths, and clarified the basic characteristics of the distortion of PO_4 groups in crystals.

The strengths of hydrogen bonds around a moiety contribute to the environmental effect. It seems to be recognized as a general rule for crystals that, when H is attached to XO_4 groups, the bond lengths are intermediate between those for the ion without the proton and those for the same ion with a residue attached (Cruickshank, 1961). However, as the effects of hydrogen-bond length are not pronounced and are

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in competition with other effects, they are sometimes obscured and have not fully been quantified. Some efforts have been made to elucidate the systematic effect of hydrogen bonding on the bond length X–O(H), where O(H) is a hydrogen-bond donor, for carboxyl groups ($X = \mathrm{C}$) (Ichikawa, 1979*a*,*b*) and for SO_4 groups ($X = \mathrm{S}$) (Catti, Ferraris & Ivaldi, 1979). Recently, Ferraris & Ivaldi (1984) extended this approach to various kinds of XO_4 and XO_3 ions, and pointed out the existence of certain correlations.

The aim of this paper is to investigate the effect of hydrogen bonding on the distortion of PO_4 tetrahedra in acid orthophosphate groups H_nPO_4 ($n = 1$-3) by examining the correlations of the distortion indices, P–O lengths, O–P–O angles and O–O lengths with hydrogen-bond lengths O···O. Discussion is confined to their O···O dependence from a purely empirical viewpoint although the geometry of coordination polyhedra has also been extensively discussed in terms of electrostatic bond strength and related concepts (*e.g.* Baur, 1970, 1974, 1981; Brown, 1981; Gibbs, Meagher, Newton & Swanson, 1981). PO_4 groups have been chosen in this study because: (*a*) most data are available for PO_4 groups among the various kinds of XO_4 ions, and (*b*) the PO_4 distortion is closely related to the phase-transition mechanism and the origin of large isotope effects on the transition temperature in some hydrogen-bonded ferroelectrics and related materials such as KH_2PO_4 (*e.g.* Lines & Glass, 1977; Tokunaga & Tatsuzaki, 1984).

The distortion of the PO_4 group is examined using three distortion indices DI defined by Baur (1974) as

$$\mathrm{DI(PO)} = \sum_{i=1}^{4} |\mathrm{PO}_i - \mathrm{PO}_m| / \sum_{i=1}^{4} \mathrm{PO}_i,$$

$$\mathrm{DI(OPO)} = \sum_{i=1}^{6} |\mathrm{OPO}_i - \mathrm{OPO}_m| / \sum_{i=1}^{6} \mathrm{OPO}_i,$$

$$\mathrm{DI(OO)} = \sum_{i=1}^{4} |\mathrm{OO}_i - \mathrm{OO}_m| / \sum_{i=1}^{4} \mathrm{OO}_i,$$

where PO_i stands for the individual distances from the tetrahedral P atom to the O atom P–O_i, OPO_i denotes individual angles $(\mathrm{O–P–O})_i$, OO_i denotes individual lengths of the tetrahedral edges $(\mathrm{O–O})_i$, and m signifies the mean values for the polyhedron. Thus the distortion indices express the average deviation of these three geometrical parameters from their means. Hereafter 'geometrical parameters' is used as a general term for the three geometrical parameters characterizing a PO_4 tetrahedron, *i.e.* P–O length, O–P–O angle and O–O distance. In the acid phosphate groups H_nPO_4 ($n = 1$-3) the O atoms are of two types: O atoms bonded to H atoms [O(H)] and O atoms not bonded to H atoms (O). The same symbol O is also used to describe both types of atoms, but when necessary a distinction will be made in order to avoid confusion.

Data collection

Data of bond lengths and angles in the tetrahedral PO_4 groups have been collected from the published literature. They include neutron diffraction as well as X-ray diffraction data. Structures in which H atoms were not located were excluded. When the relevant bond lengths and angles were not given in the literature, they were calculated from the related parameters (*i.e.* O–O from P–O and OPO *etc.*), or else from the positional coordinates [using *UNICS*, Sakurai (1967)]. Values not corrected for thermal motion were used. Data were included only if the mean estimated standard deviation of the four P–O bond lengths in a PO_4 group was less than 0·015 Å.

The site symmetry of the PO_4 group in crystals can be anywhere from 1 to $\bar{4}3m$ (the symmetry of the regular tetrahedron), but in Baur's (1974) sample 85% of the crystals had site symmetry 1. Only PO_4 groups with site symmetry 1 are studied in this paper, because when higher symmetry is present O(H) and O atoms might be replacing each other statistically. Furthermore, data were included only if the hydrogen-bond lengths were less than 2·7 Å for HPO_4 groups and their average was less than 2·7 Å for H_2PO_4 and H_3PO_4 groups. This was done because good correlations of bond lengths and angles with hydrogen-bond lengths in this range were recognized for carboxyl groups (Ichikawa, 1979*b*). A total of 25, 37 and 5 PO_4 groups were considered for HPO_4, H_2PO_4 and H_3PO_4 types, respectively.* This included data from the compilation of Ferraris & Ivaldi (1984). Baur (1974) used respectively 9, 12 and 5 PO_4 groups of each type of acid group H_nPO_4 ($n = 1, 2, 3$).

Results and discussion

Scatter diagrams of the three distortion indices, P–O lengths, O–P–O angles and O–O lengths against hydrogen-bond lengths O···O were plotted for the HPO_4 and H_2PO_4 types and some of them are shown in Figs. 1, 2, 5 and 6.* No scatter diagram is given for the H_3PO_4-type structures, since their number is too small to discuss the correlations. Linear regressions were calculated for all cases (Table 1). Nonlinear regression analysis might actually be preferred, since the longer a hydrogen bond becomes, the weaker its effects are. It also would be desirable to study the correlation with O–H bond lengths, but there was insufficient information on these.

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* A list of the structural papers used and relevant scatter diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43139 (14 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results of linear regression analysis of the* O···O *dependence of distortion indices,* P–O *lengths* (Å), OPO *angles* (°), *and* O–O *lengths* (Å) *in hydrogen-bonded* PO_4 *groups*

Intercept of regression equation = *a*; slope of regression equation = *b*; correlation coefficient = *r*; number of data used = *N*.

	a	*b*	*r*	*N*	Comments
(i) HPO_4 type					
DI(PO)	−0·1180	0·0515	0·65	24	
DI(OPO)	−0·1559	0·0686	0·66	25	
DI(OO)	−0·0216	0·0113	0·32	24	
$(P–O)_m$	1·531	0·003	0·04	24	Mean of all P–O(H) and P–O
$(OPO)_m$	110·7	−0·5	−0·38	25	Mean of all O(H)PO and OPO
$(O–O)_m$	2·530	−0·007	−0·06	24	Mean of all O(H)–O and O–O
P–O(H)	1·257	0·129	0·44	25	
P–O	1·631	−0·041	−0·44	24	Mean of three P–O
O(H)PO	129·4	−8·6	−0·56	25	Mean of three O(H)PO
OPO	90·8	8·0	0·58	25	Mean of three P–O
O(H)–O	2·668	−0·063	−0·31	24	Mean of three O(H)–O
O–O	2·421	0·038	0·24	23	Mean of three O–O
(ii) H_2PO_4 type					
DI(PO)	−0·0627	0·0319	0·27	37	Against mean of two O···O
DI(OPO)	−0·0780	0·0390	0·29	31	Against mean of two O···O
DI(OO)	−0·0388	0·0190	0·23	32	Against mean of two O···O
$(P–O)_m$	1·468	0·0262	0·21	37	
$(OPO)_m$	110·4	−0·4	−0·22	37	
$(O–O)_m$	2·432	0·028	0·14	37	
P–O(H)	1·345	0·085	0·39	73	
P–O	1·562	−0·022	−0·12	37	Mean of two P–O against mean of two O···O
O(H)PO(H)	116·7	−4·1	−0·08	37	Against mean of two O···O
O(H)PO	126·3	−6·7	−0·33	37	Mean of four O(H)PO against mean of two O···O
OPO	40·6	28·7	0·47	37	Against mean of two O···O
O(H)–O(H)	2·299	0·078	0·09	37	Against mean of two O···O
O(H)–O	2·675	−0·068	−0·18	37	Mean of four O(H)–O against mean of two O···O
O–O	1·601	0·362	0·53	37	Against mean of two O···O

HPO_4 *type*

All distortion indices correlate well with O···O and increase with increasing O···O. The slope is largest for DI(OPO) and smallest for DI(OO), in accordance with Baur's (1974) conclusion (case II of Table 2). The mean values of the P–O lengths, OPO angles and O–O lengths of the HPO_4 type on the other hand are not correlated at all with O···O lengths (Table 1) (see the more detailed discussion below).

With increasing O···O the P–O(H) length increases, whereas the average of the three P–O lengths decreases slightly, thus maintaining a constant P–O value in the tetrahedron. The upper half of Fig. 1 corresponds to part of Fig. 1(*e*) of Ferraris & Ivaldi (1984). Analogously to the P–O lengths, the mean of the three O(H)PO angles in the HPO_4 type follows a different trend from the mean of the three OPO angles (Fig. 2). The former are smaller than the tetrahedral angle (109·5°) and the latter are larger, as has already been observed by Baur & Khan (1970). However, individual values of O(H)PO and OPO overlap in their values. With increasing O···O the mean O(H)PO decreases, whereas the mean OPO increases, conserving the mean value of the six OPO angles. As for O–O lengths, the overall mean O(H)–O length is shorter than the overall mean O–O length, but the individual mean values overlap. The mean value of the six O–O lengths stays constant. Thus the PO_4 distortion of the HPO_4 type becomes large with increasing O···O and is characterized approximately by the shift of the P atom away from the centroid of a regular tetrahedral framework of O atoms while retaining site symmetry $3m$ (Fig. 3*a*).

Table 2. *Average values of the three distortion indices and the three structural parameters for* H_nPO_4 (n=1–3)

N is the number of PO_4 groups used in averaging.

	HPO_4(*N*)	H_2PO_4(*N*)	H_3PO_4(*N*)	PO_4*(*N*)
DI(PO)	0·0171 (25)	0·0192 (32)	0·0138 (5)	0·005 (35)
DI(OPO)	0·0235 (25)	0·0233 (32)	0·0270 (5)	0·009 (35)
DI(OO)	0·0082 (25)	0·0102 (32)	0·0144 (5)	0·006 (35)
P–O (Å)	1·540 (25)	1·536 (37)	1·531 (5)	1·533 (35)
OPO (°)	109·4 (25)	109·4 (37)	109·4 (5)	109·5 (35)
O–O (Å)	2·513 (25)	2·505 (37)	2·498 (5)	2·504 (35)

* Baur (1974), no edge sharing.

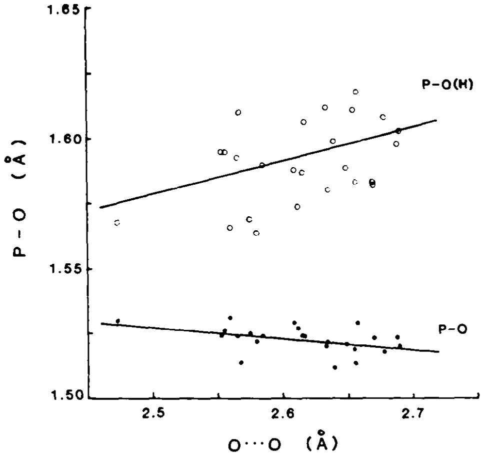


Fig. 1. Scatter diagram of P–O bond lengths of HPO_4-type tetrahedra against hydrogen-bond lengths O···O. Open and filled circles represent P–O(H) [O(H): hydrogen-bond donor] and the mean of the three P–O, respectively.

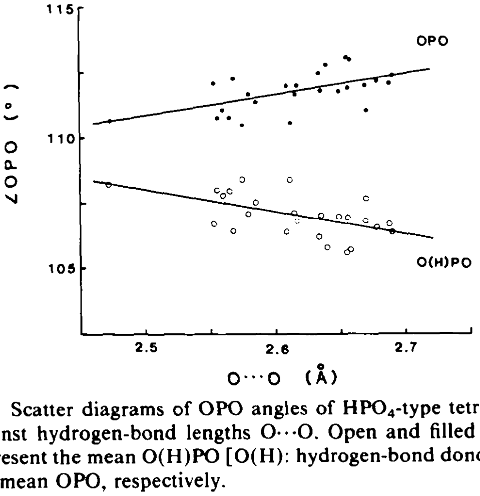


Fig. 2. Scatter diagrams of OPO angles of HPO_4-type tetrahedra against hydrogen-bond lengths O···O. Open and filled circles represent the mean O(H)PO [O(H): hydrogen-bond donor] and the mean OPO, respectively.

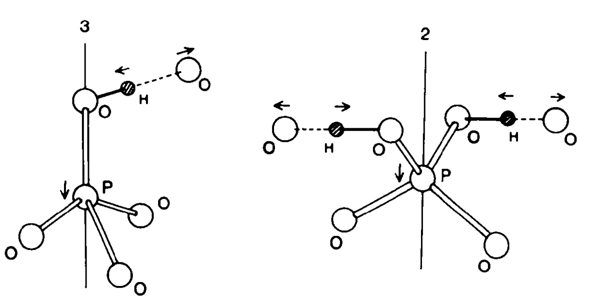
H_2PO_4 *type*

The tetrahedral distortion of the H_2PO_4 type is more complicated than that of the HPO_4 type, because two O(H) atoms donate hydrogen bonds and each geometrical parameter is influenced by each of the two hydrogen bonds, and moreover the relative geometrical arrangement of these bonds in the crystal (Fig. 3*b*) affects the values of some generated parameters. The correlations in the H_2PO_4 type are generally less clear than those in the HPO_4 type.

The longer bonds $(O\cdots O)_L$ and the shorter bonds $(O\cdots O)_S$ differ in length from 0·002 to 0·178 Å (Fig. 4). For 85% of the H_2PO_4 groups the difference is less than 0.08 Å. Thus it can be said that H_2PO_4 groups in crystals favor equal hydrogen-bond lengths. In the following correlation the mean of $(O\cdots O)_S$ and $(O\cdots O)_L$ is used $[(O\cdots O)_{av}]$.

All three distortion indices correlate with $(O\cdots O)_{av}$ and increase with increasing $(O\cdots O)_{av}$. DI(OO) shows a stronger $(O\cdots O)_{av}$ dependence in the H_2PO_4 type than in the HPO_4 type, but its magnitude is still smaller than DI(PO) and DI(OPO). Thus the same distortion pattern is seen as in the HPO_4 type.

Some of the H_2PO_4 groups clearly showed higher DI(OPO) and DI(OO) values. This happens in PO_4 groups where two O atoms coordinate to the same cation, *i.e.* an O–O edge of PO_4 is shared with a divalent-cation coordination polyhedron (Pauling, 1960; Baur, 1974). This leads to longer P–O lengths, smaller OPO angles and shorter O–O lengths. Among the structures studied, this 'edge-sharing' coordination and its effects are discussed in $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971), $Ca(H_2PO_4)_2$ (Dickens, Prince, Schroeder & Brown, 1973), orthorhombic $Ba(H_2PO_4)_2$ (Gilbert, Lenhert & Wilson, 1977; Prelesnik, Herak, Čurić & Krstanović, 1978), triclinic $Ba(H_2PO_4)_2$ (Gilbert & Lenhert, 1978) and $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ (Takagi, Mathew & Brown, 1980). These were not included in the DI(OPO) and DI(OO) diagrams. The shared edges are also found in some of the HPO_4 groups, but do not have higher values of the distortion indices.



(*a*) HPO_4 (3*m*) (*b*) H_2PO_4 (*mm*2)

Fig. 3. An illustration of the hydrogen-bond-length dependence of the PO_4 distortion for (*a*) HPO_4- and (*b*) H_2PO_4-type tetrahedra.

As with the HPO_4-type structures, we were unable to find any definite O···O dependence in the mean P–O, OPO and O–O values in the H_2PO_4 type. The regression lines of mean P–O and O–O appear to exhibit a slight increase with an increase of O···O, but it is hardly significant. It is noted, however, that this trend is consistent with Baur's (1974, 1981) statement that the mean P–O length increases slightly with an increase of the DI(PO), since the same result can be obtained by combining $(P–O)_m$ *vs* O···O and DI(PO) *vs* O···O correlation. In Fig. 5, P–O(H) is plotted against the hydrogen-bond length which each O(H) donates, and an average of the two P–O lengths is plotted against $(O\cdots O)_{av}$. The upper part of Fig. 5 corresponds to part of Fig. 1(*e*) in Ferraris & Ivaldi (1984). With increasing O···O, P–O(H) increases and P–O appears to decrease only slightly, retaining the mean P–O distance within an H_2PO_4 group constant.

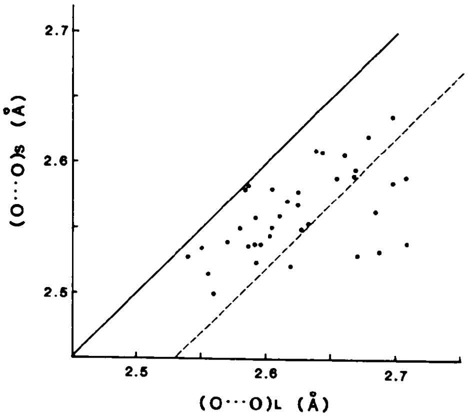


Fig. 4. Scatter diagram of the two hydrogen-bond lengths in the H_2PO_4 group. $(O\cdots O)_L$ and $(O\cdots O)_S$ denote the long and short bonds, respectively. Solid and broken straight lines represent the case of $(O\cdots O)_L=(O\cdots O)_S$ and $(O\cdots O)_L-(O\cdots O)_S=0{\cdot}08$ Å, respectively (see text).

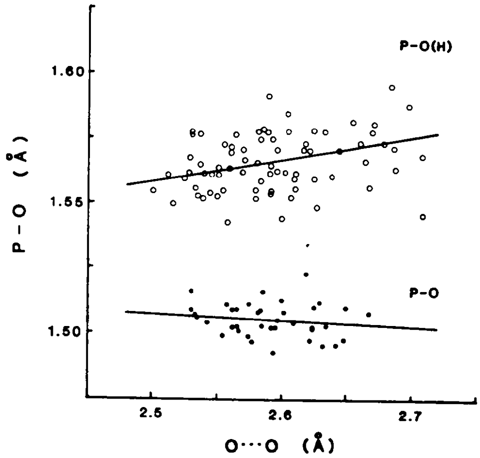


Fig. 5. Scatter diagrams of P–O bond lengths in H_2PO_4-type tetrahedra against hydrogen-bond lengths O···O. The hydrogen-bond lengths are O(H)-participated individual bonds for P–O(H) (open circles) and the mean of two hydrogen bonds for P–O (filled circles).

The six OPO angles in an H_2PO_4 group consist of one O(H)PO(H), one OPO and four O(H)PO angles. Their scatter diagrams against $(O\cdots O)_{av}$ are shown in Fig. 6, where the average value is plotted for O(H)PO. It may be seen that O(H)PO(H) < O(H)PO < OPO forms a whole. The averaged O(H)PO are separated from OPO, but continue on O(H)P(H)O. On examining the individual O(H)PO values, we find that they are separated from OPO as well, but overlap with each other to O(H)P(H)O. These results indicate that the statement of Baur & Khan (1970) is only approximately valid; they argued that the angles of H_2PO_4 fall neatly into three categories: greater than, about equal to, and smaller than the tetrahedral angle. As O···O increases, OPO also increases, whereas the averaged O(H)PO appears to decrease slightly. O(H)PO(H) data are too scattered for us to find any O···O dependence. The reason for this scattering seems to be at least partly because the configuration of two hydrogen bonds, *i.e.* the H–O–P–O–H torsion angle, in each H_2PO_4 group varies greatly from crystal to crystal.

Like the OPO angles, the six O–O lengths in the H_2PO_4 group are classified into three groups. Scatter of data is more pronounced in the O–O lengths than in the OPO angles. The data scattering is at least partly due to the same origin as in the OPO case.

Summing up the characteristics of PO_4 distortion in H_2PO_4-type structures, it can be said that the distortion becomes large with an increase of O···O, approximately in such a way that the P atom moves far from the centroid of the regular tetrahedral oxygen framework while maintaining site symmetry *mm*2 (Fig. 3*b*).

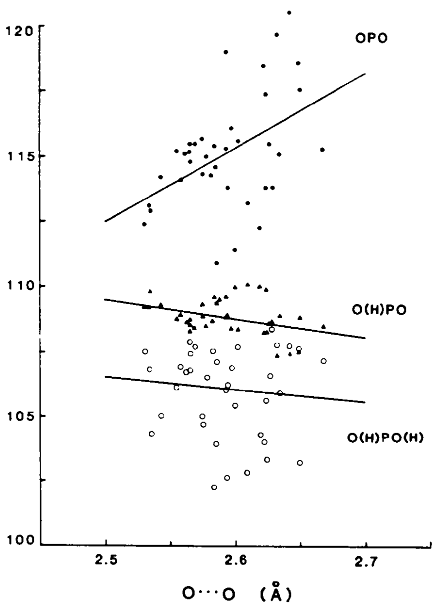


Fig. 6. Scatter diagrams of OPO angles in H_2PO_4-type tetrahedra against the mean length of two hydrogen bonds O···O. Open circles, triangles and filled circles represent O(H)PO(H) [O(H): hydrogen-bond donor], the mean of four O(H)PO and OPO, respectively.

H_3PO_4 *type*

Only five tetrahedra are available at present for the H_3PO_4 type and are too limited to form scatter diagrams. Nothing can therefore be concluded about the O···O dependence of the three distortion indices. The average values of P–O, OPO and O–O also seem to retain constancy for the H_3PO_4 type. The P–O lengths and OPO angles are clearly separated into two groups as in the HPO_4 and H_2PO_4 types. Jönsson (1972) pointed out that the OPO angles in H_3PO_4 groups are expected to fall into two classes: the O(H)PO(H) angles should be smaller than the tetrahedral angle, whereas the O(H)PO angles should be larger and that is true for all the individual bond angles. The present examination indicates that his statement is valid, not strictly but as a general trend.

Comparison among H_nPO_4 *types*

The average values of the three distortion indices and the three geometrical parameters for the H_nPO_4 ($n = 1$-3) types are given in Table 2. DI(PO) and DI(OO) are larger in the H_2PO_4 than in the HPO_4 type, whereas the DI(OPO) is almost the same. It can therefore be said that the distortion of PO_4 is larger in H_2PO_4 than in HPO_4. Table 2 also gives the corresponding mean values for the PO_4 groups without any H atom. As expected, it is seen that the three distortion indices are larger than in the acid phosphate PO_4 groups than in the PO_4 groups without an H atom.

On the other hand, the constancy of the mean P–O length has been known and discussed for a long time (Cruickshank, 1961; Baur 1970), but there is still some argument about the degree of its validity (Baur & Khan, 1970). It may thus be worth emphasizing that the mean values of the three geometrical parameters are excellently preserved in each H_nPO_4 type, in addition to their lack of appreciable O···O dependence, discussed earlier. With respect to OPO angles, 24 data out of 25 (96%) for HPO_4, 31 data out of 33 (94%) for H_2PO_4 and all 5 data for H_3PO_4 fall within 109·4 (1)° (0·1%). As for the P–O lengths, 19 data out of 25 (76%) for HPO_4, 27 data out of 37 (73%) for H_2PO_4, and 2 data out of 5 for H_3PO_4 fall within ±0·004 Å of their respective mean value (0·3%). For the O–O lengths, 21 data out of 25 (84%) for HPO_4, 31 data out of 37 (84%) for H_2PO_4, and 3 data out of 5 for H_3PO_4 fall within ±0·008 Å of their respective mean value (0·3%). The trend indicates that the mean P–O length decreases as PO_4 varies from HPO_4 to H_3PO_4 and that, corresponding to P–O, O–O also decreases. This trend can also be seen in Baur's (1974) data (Table 13).

The main conclusions to emerge from this study can be summarized as follows:

(*a*) All the distortion indices DI(PO), DI(OPO) and DI(OO) for the HPO_4 and H_2PO_4 types correlate with O···O and show an increase with increasing O···O. The magnitude and variation of DI(OO) is small compared with those of the DI(PO) and DI(OPO).

(*b*) The mean values of P–O, OPO and O–O are preserved for each H_nPO_4 group.

(*c*) The correlation is less clear in the H_2PO_4 than in the HPO_4 type, partly because the mutual configuration of the two hydrogen bonds affects the values of the geometrical parameters and obscures the correlations.

(*d*) The O···O dependence of the PO_4 distortion is approximately described by a model in which with increasing O···O the P atom moves in a direction away from the centroid of the regular tetrahedral framework of O atoms, while retaining $3m$ site symmetry for the HPO_4 type (Fig. 3*a*) and $mm2$ site symmetry for the H_2PO_4 type (Fig. 3*b*).

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A Structural Analysis of Potassium, Rubidium and Caesium Substitution in Barium Hollandite

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Abstract

The changes in crystal structure of the barium hollandite $Ba_x(Al_{2x}Ti_{8-2x})O_{16}$ ($x = 1{\cdot}11$ and $1{\cdot}24$) with barium being partially substituted by K, Rb or Cs, have been determined using the Rietveld method on high-resolution neutron powder diffraction data. When K and Rb are substituted, solid solutions form with compositions conforming to a linear combination of the end members $Ba_{1\cdot24}(Al_{2\cdot48}Ti_{5\cdot52})O_{16}$ and $Rb_{1\cdot5}$ or $K_{1\cdot5}(Al_{1\cdot5}Ti_{6\cdot5})O_{16}$. Cs substitution however, is limited to approximately 0.25 Cs ions per unit cell for specimens prepared in air at atmospheric pressure. The compositions in this range can be described as a linear combination of the end members $Ba_{1\cdot11}(Al_{2\cdot22}Ti_{5\cdot78})O_{16}$ and $Cs_{1\cdot32}(Al_{1\cdot32}Ti_{6\cdot68})O_{16}$. This limit is imposed by the large size of Cs which prevents the ion occupying sites in the *c*-axis tunnels next to

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