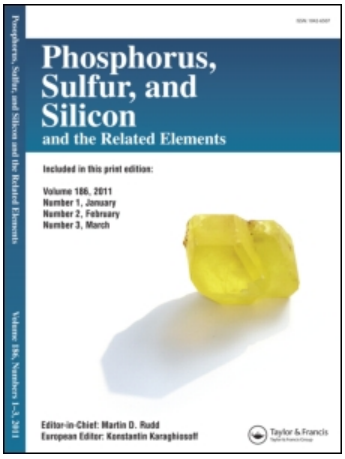

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Refinement by Neutron Diffraction of the Crystal Structure of Hydroxyethylidene Bisphosphonic ACID Monohydrate: C(CH 3)(OH)(PO 3 H 2) 2 ·H 2 O

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REFINEMENT BY NEUTRON DIFFRACTION OF THE CRYSTAL STRUCTURE OF HYDROXYETHYLIDENE BISPHOSPHONIC ACID MONOHYDRATE: $C(CH_3)(OH)(PO_3H_2)_2 \cdot H_2O$

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The neutron diffraction study of the crystal structure of $C(CH_3)(OH)(PO_3H_2)_2 \cdot H_2O$ *carried out at room temperature led to a least squares refinement based on 949 reflections with* $R(F^2) = 0.0471$ *and* $R_w(F^2) = 0.0473$. *This compound crystallizes with the monoclinic* $P2_1/c$ *(n°14) space group and* $a = 6.983(3)\text{Å}$, $b = 17.56(3)\text{Å}$, $c = 7.109(9)\text{Å}$, $\beta = 108.5(1)°$, $V = 826.4\text{Å}^3$, *and* $Z = 4$. *This investigation gives precise details about the hydrogen atom positions, the hydrogen bonds, and the configuration of the hydroxyethylidene bisphosphonic molecule which is then compared to that of the rubidium salt previously studied also by neutron diffraction.*[2]

Keywords: Crystal structure by neutron diffraction; hydroxyethylidenebisphosphonic acid

INTRODUCTION

The crystal structure of $C(CH_3)(OH)(PO_3H_2)_2 \cdot H_2O$ ($HEBP.H_2O$) was firstly investigated by x-ray diffraction by Uchtman and Gloss.[1] Very soon after the discovery of the hydroxybisphosphonic function, its complexation power of highly electropositive metal cations was demonstrated.[3–7] Therefore, the properties of this function appear very

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interesting for different industrial applications such as detoxycation of industrial effluents and recovery of valorizable metals[8,10] and medical applications such as treatment of Paget's disease of bone, cancer-related hypercalcemie, and postmenoposal osteoporosis.[11–13]

Since this first crystal structure determination, more than 60 other crystal structure determinations have been solved for different hydroxybisphosphonates of metallic and organic cations.[14] These studies show the great flexibility of the hydroxybisphosphonic function because its different possibilities of ionization degrees and its various complexation modes.

The aim of this work is to give precise details about the hydrogen atom positions, the hydrogen bonds, and the configuration of the hydroxyethylidenebisphosphonic molecule in order to understand the structural modifications in the cation complexation process.

RESULTS AND DISCUSSION

The morphology of the single crystal used is given in Figure 1.

The effective linear absorption coefficient was determined experimentally (1.94 cm^{-1}). Integrated reflection intensities evaluated by the method of Lehman and Larsen[17] (program *NDATRED*) were corrected for Lorentz and absorption effects (gaussian grid $6 \times 8 \times 6$). Isotropic type I extinction corrections with Lorentzian mosaic distribution were applied. The neutron scattering lengths used[18] were (in fm): $b_P = 5.13$, $b_O = 5.803$, $b_C = 6.648$, and $b_H = 3.741$. Initial coordinates of non hydrogen atoms were taken from the room temperature x-ray model.[1]

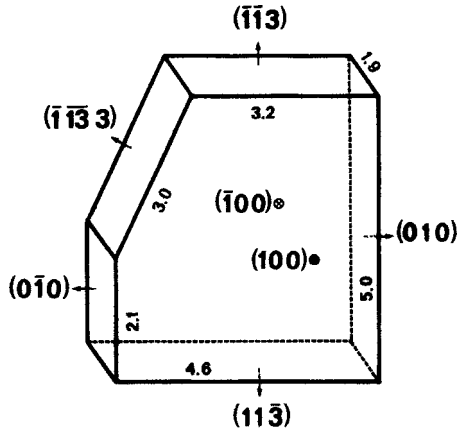

FIGURE 1 Morphology of the HEBP.H_2O single crystal used for neutron diffraction study (length in mm).

All hydrogen atoms were located from a Fourier-difference synthesis. A final series of three refinement cycles of the atomic coordinates and of the anisotropic thermal parameters using the *CRYSTAL* program[15] gave $R = 0.0471$, $R_w = 0.0473$, and $GFIT = 1.04$. The figures were obtained with the Ortep-3 for Windows (Version 1.05) program.[16] The experimental and refinement conditions are given in Table I. Table II

TABLE I Experimental and Refinement Conditions

Neutron source	Hot source Orphee Reactor (Laboratoire Leon Brilloin C.E.A.-C.N.R.S., CEN-Saclay)
Monochromator	Cu(220), Er filter (0.25 mm)
Wavelength (Å)	0.83080
Temperature (K)	293
Formula unit	$C(CH_3)(OH)(PO_3H_2)_2,H_2O$
Formula weight (g mol^{-1})	224.04
Space group	$P2_{1/C}$ (n°14)
Cell parameters	
a(Å)	6.983(9)
b(Å)	17.556(3)
c(Å)	7.109(9)
β(°)	108.5(1)
Volume ($Å^3$)	826.4
Z	4
d calcd. (g.cm^{-3})	1.80
Crystal volume (mm^3)	39.4
Boundary faces	(100), (−100), (010), (0–10), (−1–13), (11–3), (−1–133)
Reciprocal space	$-10 \le h \le 10$; $-20 \le k \le 26$; $0 \le 1 \le 10$
Scan mode	ω for $3.0° < 2\theta < 50.0°$; ω/θ for $50.0° < 2\theta < 75.0°$
Scan width	$\Delta\omega^2 = 9 - 27\mathrm{tg}\theta + 40\mathrm{tg}^2\theta$ for $2\theta < 50°$ $\Delta\omega^2 = 9 - 27\mathrm{tg}\theta + 44\mathrm{tg}^2\theta$ for $2\theta > 50°$
Reference reflections	204, 640, 1132
Linear absorption coef. (cm^{-1})	1.94
Absorption correction	no
F(000)	139.8
Measured reflections	5,169
Unique reflections	3,175
Reflexions used in final refinement $I_o \ge 2\sigma(I_o)$	1874
Agreement factors	
Internal $R_{int} = \sum \lvert F_o^2 - F_{c(av)}^2 \rvert / \sum F_o^2$	0.03624
$R(F^2) = \sum \lvert F_{o2} - k^2 F_c^2 \rvert / \sum F_o^2$	0.04708
$R_w(F^2) = \left[\sum_w (F_o^2 - k^2 Fc^2)^2 / \sum_w F_o^4 \right]^{1/2}$	0.04732
$S = \left[\sum_w (F_o^2 - k^2 Fc^2)^2 / (m - n) \right]^{1/2}$	1.03679

TABLE II Atomic Coordinates and Equivalent Isotropic Thermal Parameters; Estimated Standard Deviations in Parenthesis.
$<U> = 1/3\sum U_{ij}(a_j \times b_j)(a_j^* \times b_j^*)$

Atom	X	Y	Z	<U>
P1	0.8025(2)	0.40891(6)	−0.0425(2)	0.0146
P2	0.6217(2)	0.36647(6)	0.2868(2)	0.0154
C1	0.8430(1)	0.36488(5)	0.2004(1)	0.0141
C2	1.0185(2)	0.40562(6)	0.3532(1)	0.0237
O1	0.7440(2)	0.49077(6)	−0.0380(2)	0.0221
O2	0.6424(2)	0.35922(7)	−0.1887(2)	0.0231
O3	1.0014(2)	0.39812(7)	−0.0933(2)	0.0245
O4	0.5693(2)	0.45091(7)	0.3077(2)	0.0276
O5	0.4493(2)	0.32715(8)	0.1267(2)	0.0248
O6	0.6759(2)	0.32745(7)	0.4838(2)	0.0226
O7	0.8995(2)	0.28714(6)	0.1927(2)	0.0199
Ow	0.2627(2)	0.22574(8)	0.2254(2)	0.0282
H2	0.6538(3)	0.3500(1)	−0.3299(3)	0.0277
H3	1.1031(4)	0.4398(1)	−0.0448(4)	0.0306
H4	0.4558(4)	0.4744(1)	0.2002(4)	0.0336
H5	0.3672(4)	0.2808(2)	0.1785(3)	0.0345
H7	0.7996(4)	0.2575(1)	0.0927(3)	0.0293
H8	1.0455(6)	0.3815(3)	0.4973(4)	0.0570
H9	0.9867(6)	0.4655(2)	0.3592(6)	0.0546
H10	1.1553(5)	0.4001(3)	0.3131(6)	0.0554
H1w	0.1346(4)	0.2449(2)	0.2369(5)	0.0404
H2w	0.3350(5)	0.1984(2)	0.3424(5)	0.0507

gives the fractional atomic coordinates and the equivalent isotropic thermal parameters. Anisotropic thermal parameters for all the atoms are given in Table III. Selected bond lengths and valence angles are compiled in Table IV.

Alone in a infinitely diluted medium the HEBP molecule presents the possibility of many free rotations. This is the case of each PO_3H_2 group, CH_3, and H atoms of the P—OH groups. In these conditions, this molecule would show a symmetry plane defined by O7—C1—C2. But in the crystallized state, all free rotations are locked by intermolecular hydrogen bonds or hydrogen bonds involving water molecules or by the complexation of cations in salts. Thus, the loss of the symmetry plane is systematically observed. In the case of the crystallized HEBP·H_2O, the free rotations are locked only by hydrogen bonds which are relatively weak constraints. Nevertheless these bonds induce the dissymmetry between the two phosphonic groups (Figure 2a). Apart some small deformations the loss of the symmetry plane is due to a rotation of 120° of one of the PO_3H_2 groups with regard to the other. For example a

TABLE III Anisotropic Thermal Parameters ($\times 10^3$)*

Atom	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
P1	16.4(4)	13.4(5)	14.6(4)	−0.0(3)	5.7(3)	−2.1(3)
P2	19.3(5)	16.0(5)	11.5(4)	1.0(3)	5.5(3)	2.9(3)
C1	14.9(3)	12.5(3)	13.9(3)	−0.5(2)	3.3(2)	0.1(2)
C2	23.9(4)	22.7(5)	19.2(4)	−2.8(3)	−0.5(3)	−4.5(3)
O1	23.3(5)	14.4(5)	27.8(5)	4.1(3)	6.9(4)	1.1(3)
O2	24.7(5)	30.0(6)	16.0(4)	−7.6(4)	8.3(3)	−10.9(4)
O3	23.8(5)	23.6(5)	31.0(5)	−5.1(4)	15.8(4)	−3.8(4)
O4	35.1(6)	21.7(5)	25.3(5)	−0.6(4)	8.5(4)	11.7(5)
O5	22.1(5)	35.6(6)	15.6(4)	−0.6(4)	4.5(3)	−6.4(4)
O6	34.0(6)	22.3(5)	13.1(4)	2.9(3)	9.7(4)	5.0(4)
O7	19.6(4)	12.0(4)	26.7(5)	−1.2(3)	5.5(3)	2.2(3)
Ow	20.6(5)	28.4(6)	35.3(6)	3.1(5)	8.3(4)	0.1(4)
H2	33(1)	27.4(9)	23.1(8)	−2.5(7)	9.1(7)	−3.7(7)
H3	29(1)	28(1)	37(1)	−1.3(8)	14.5(8)	−3.6(6)
H4	41(1)	27(1)	34(1)	8.6(8)	13.7(9)	11.0(9)
H5	29(1)	42(1)	31(1)	−4.9(9)	6.8(7)	2.4(9)
H7	33(1)	19.8(9)	33.4(9)	−7.4(7)	8.5(8)	−2.2(7)
H8	62(2)	67(2)	25(1)	10(1)	−10(1)	−23(2)
H9	64(2)	29(1)	54(2)	−13(1)	−6(1)	−3(1)
H10	28(1)	77(2)	61(2)	−18(2)	13(1)	−13(1)
H1w	29(1)	45(1)	51(1)	−2(1)	19(1)	0.3(9)
H2w	45(2)	46(2)	57(2)	20(1)	11(1)	4(1)

*Estimated standard deviations in parenthesis.

rotation of 120° of the $P2O_3H_2$ group from its initial position gives a configuration with a quasi plane of symmetry (Figure 2b).

The Table V gives different pseudo torsion angles. $C2H_3$ and P1—C1(O7)—P2 are in a quasi ideal staggered configuration (Figure 3a) as $P1O_3$ with P2—C1(O7)—C2 (Figure 3b) and as $P2O_3$ with P1—C1(O7)—C2 (Figure 3c). On the other hand, $C2H_3$ with $P1O_3$ (Figure 3d) and $C2H_3$ with $P2O_3$ (Figure 3e) are in a quasi-ideal eclipsed configuration. Lastly the two phosphonic groups are very near of an eclipsed configuration (Figure 3f). All these configurations are normally expected are very weakly distorted: It is a consequence and the confirmation that the cohesion between the HEBP molecules in the crystallized state is assumed only by weak bonds. For comparison the Table V gives also the pseudotorsion angles for the hydroxybisphosphonate ligand in the rubidium salt. They are calculated from the atomic positions obtained by neutron diffraction.[2] It can be observed the great influence of the cation on the relative position of the two phosphonate groups (average shiftings: 2.7° for $HEBP.H_2O$; 16.1° for the Rb salt). The relative positions of the other tetrahedral groups are generally less perturbed.

TABLE IV Main Interatomic Distances (Å) and Main Valence Angles (°)*

Coordinat $HEBP^{3-}$			
C1—O7	1.426(1)	P1—O2	1.534(2)
C1—C2	1.532(1)	P1—O3	1.554(2)
C1—P1	1.830(1)	P2—O4	1.545(2)
C1—P2	1.835(1)	P2—O5	1.534(2)
P1—O1	1.497(2)	P2—O6	1.496(1)
P1—C1—P2	114.52(6)	C2—C1—O7	107.76(8)
P1—C1—C2	108.71(7)	P2—C1—C2	108.94(7)
P1—C1—O7	109.25(7)	P2—C1—O7	107.46(8)
O1—P1—O2	114.6(1)	O4—P2—O5	110.4(1)
O1—P1—O3	113.07(9)	O4—P2—O6	110.28(9)
O2—P1—O3	106.62(9)	O5—P2—O6	113.2(1)
O1—P1—C1	110.30(8)	O4—P2—C1	107.28(9)
O2—P1—C1	105.09(8)	O5—P2—C1	106.92(8)
O3—P1—C1	106.62(8)	O6—P2—C1	108.48(8)
C2—H8	1.068(3)	O3—H3	1.002(3)
C2—H9	1.077(3)	O4—H4	0.998(3)
C2—H10	1.085(3)	O5—H5	1.122(3)
O2—H2	1.045(2)	O7—H7	0.973(2)
Ow—H1w	0.983(3)	Ow—H2w	0.955(3)
C1—C2—H8	110.6(2)	H8—C2—H9	108.9(4)
C1—C2—H9	110.8(2)	H8—C2—H10	108.3(4)
C1—C2—H10	110.2(2)	H9—C2—H10	107.8(4)
P1—O2—H2	118.6(2)	P2—O5—H5	116.4(1)
P1—O3—H3	114.8(2)	P2—O4—H4	118.5(2)
C1—O7—H7	113.3(2)	H1w—Ow—H2w	110.1(3)

Hydrogen bonds

Symmetry code: x, y, z − 1; [i]: −x, −y, −z; [iii]: x, 0.5 − y, 1.5 + z; *: x, y, z + 1; [i*]: −x, −y, −z − 1.

A H B	A—H	A—B	H—B	A—Ĥ—B
O2—H2·····O6*	1.046(2)	2.476(2)	1.437(2)	172.7(2)
O3—H3·····$O1^{i}$	1.003(3)	2.604(2)	1.604(3)	176.4(2)
O4—H4·····$O1^{i}$	0.999(3)	2.617(2)	1.622(3)	174.0(3)
O5—H5·····Ow	1.121(3)	2.437(2)	1.317(3)	175.8(2)
$O7^{i*}$.—.$H7^{i*}$····O6	0.974(2)	2.687(2)	1.771(3)	154.8(2)
Ow—H1w·····O7	0.984(3)	2.697(2)	1.737(3)	164.5(3)
Ow—H2w·····$O5^{iii}$	0.955(3)	2.888(2)	1.974(4)	159.5(4)

*Estimated standard deviations in parenthesis.

The Table VI gives some interesting atomic planes in the HEBP molecule. It can be observed that the oxygen atoms O3 and O6 are very near to the P1—C1—P2 plane, and H7 and H9 very near to the C2—C1—O7 plane, whereas H2 is clearly out of the O1—P2—O2 plane as well as H5 with the O4—P2—O5 plane.

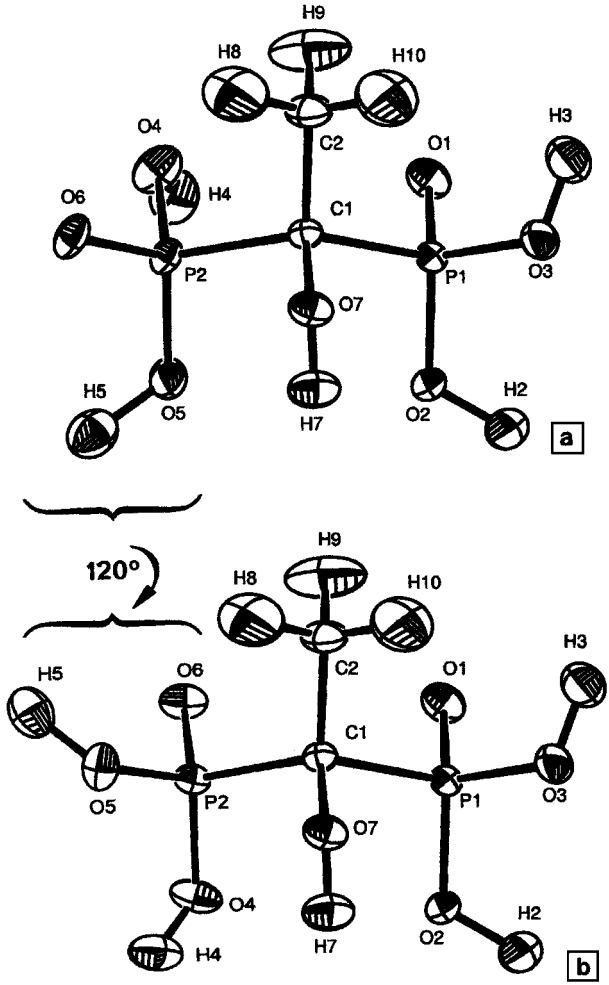

FIGURE 2 (a) Configuration of the HEBP molecule in the crystallized state; (b) Configuration showing a quasi plane of symmetry of the HEBP molecule artificially obtained after a rotation of 120° of the $P2O_3H_2$ group from the real configuration (a).

The Figure 4 shows a general view of the crystal structure with the network of hydrogen bonds. They occur only between HEBP molecules or between a HEBP molecule and a water molecule and assume the three dimensional cohesion. There is no hydrogen bond between two water molecules and no intramolecular hydrogen bond, notwithstanding, a variety of hydrogen bonds with different strengths are still observed (Table IV). The proton position (H), precisely determined by

TABLE V Comparison Between the Pseudo-Torsion Angles (°) for Bisphosphonyle Group (Estimated Standard Deviations in Parenthesis) in the HEBP·H_2O and Rb(HEBP)·$2H_2O$ Crystal Structures Solved by Neutron Diffraction

	HEBP·H_2O	Rb(HEBP)·$2H_2O$
O1—P1 P2—O4	−3.3(1)	15.3(1)
O2—P1 P2—O5	−7.4(1)	13.6(1)
O3—P1 P2—O6	2.6(1)	19.5(1)
C1—P2 C2—H8	−49.6(2)	−56.8(1)
C1—O7 C2—H9	−174.8(3)	170.0(2)
C1—P1 C2—H10	54.8(2)	48.5(2)
C2—H8 P1—O2	8.3(3)	11.0(3)
C2—H9 P1—O1	3.5(2)	12.4(2)
C2—H10 P1—O3	−2.1(3)	16.2(2)
C2—H8 P2—O6	5.2(3)	6.3(2)
C2—H9 P2—O4	3.9(2)	9.6(2)
C2—H10 P2—O5	11.3(3)	23.0(2)
C2—C1 P1—O1	56.3(1)	47.2(1)
C2—C1 P1—O2	171.1(1)	178.6(1)
C2—C1 P1—O3	56.8(1)	63.4(1)
C1—O7 P1—O1	179.5(1)	170.5(1)
C1—O7 P1—O2	53.6(1)	52.4(1)
C1—O7 P1—O3	53.1(1)	53.7(1)
C2—C1 P2—O4	55.8(1)	61.5(1)
C2—C1 P2—O5	177.8(1)	158.3(1)
C2—C1 P2—O6	54.5(1)	51.1(1)
C1—O7 P2—O4	175.0(1)	165.0(1)
C1—O7 P2—O5	60.2(1)	42.3(1)
C1—O7 P2—O6	53.0(1)	62.8(1)

neutron diffraction single crystal data, enables us to give interesting comparison of O—H bond lengths of the hydrogen bonds usually discussed in terms of A–B distances in most x-ray reports. First, it can be observed that except in the hydrogen bonds involving the water molecule and the alcohol function, the hydrogen bonds studied here, A—H·····B are quasi-linear (Table IV). The O2—H2·····O6* is very strong (2.476(2)Å). The strongest H-bond O5—H5·····Ow is related with an unusually long O5—H5 bond distance of 1.121(3)Å combined with a small inclination of the O5—H5·····Ow angle (175.8(2)°). Nethertheless, it cannot be considered that the water molecule is ionized as an oxonium $H3O^+$ cation[19] as it was found in the case of 1,6-dihydroxyhexylidene-1,1,6,6-tetraphosphonic $(H_3O)_2[(H_3O_6P_2)C(OH)]_2(CH_2)_4{\cdot}2H_2O$, isostructural with the potassium salt $K_2[(H_3O_6P_2)C(OH)]_2(CH_2)_4{\cdot}2H_2O$. But even in this very special case a complete hydrogen ordering in an asymmetric H-bond was still observed.

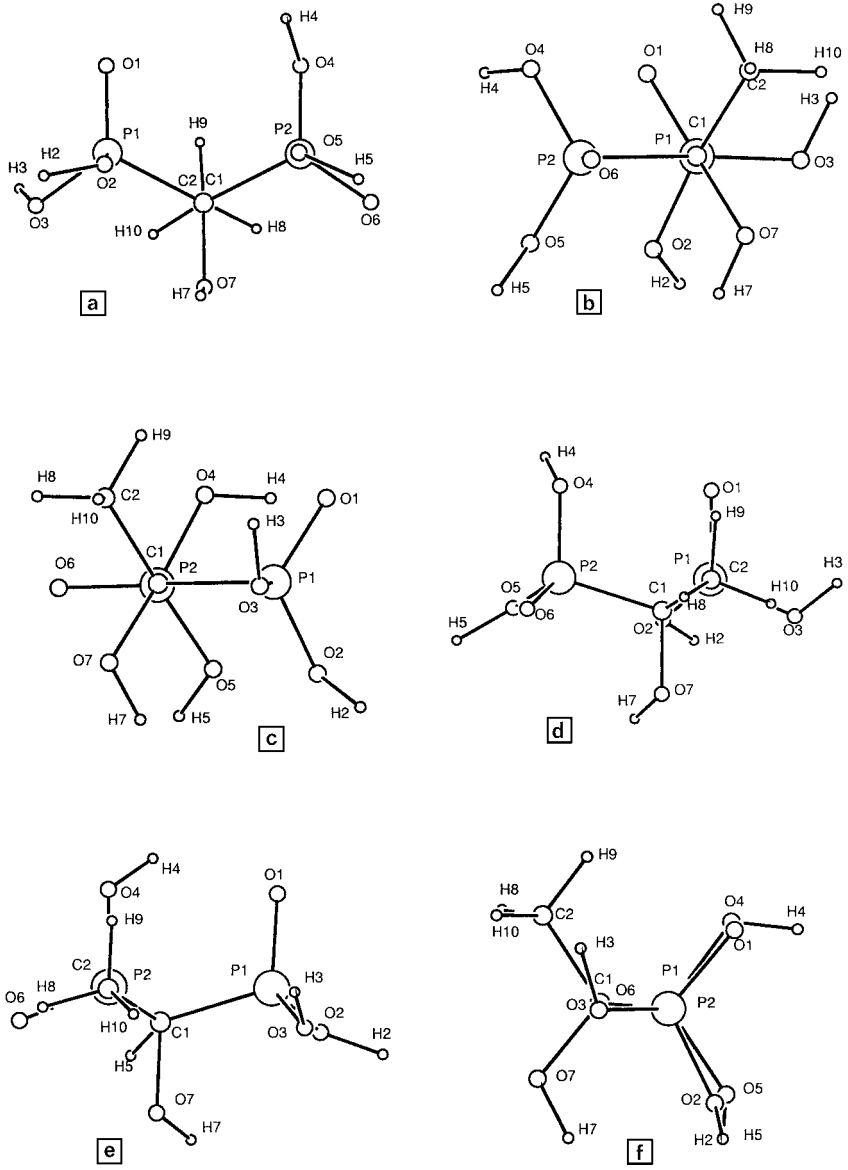

FIGURE 3 (a) Staggered configuration between $C2H_3$ and P1—C1(O7)—P2 groups; (b) Staggered configuration between $P1O_3$ and P2—C1(O7)—C2 groups; (c) Staggered configuration between $P2O_3$ and P1—C1(O7)—C2 groups; (d) Eclipsed configuration between $C2H_3$ and $P1O_3$ groups; (e) Eclipsed configuration between $C2H_3$ and $P2O_3$ groups; (f) Shifting between $P1O_3$ and $P2O_3$ groups.

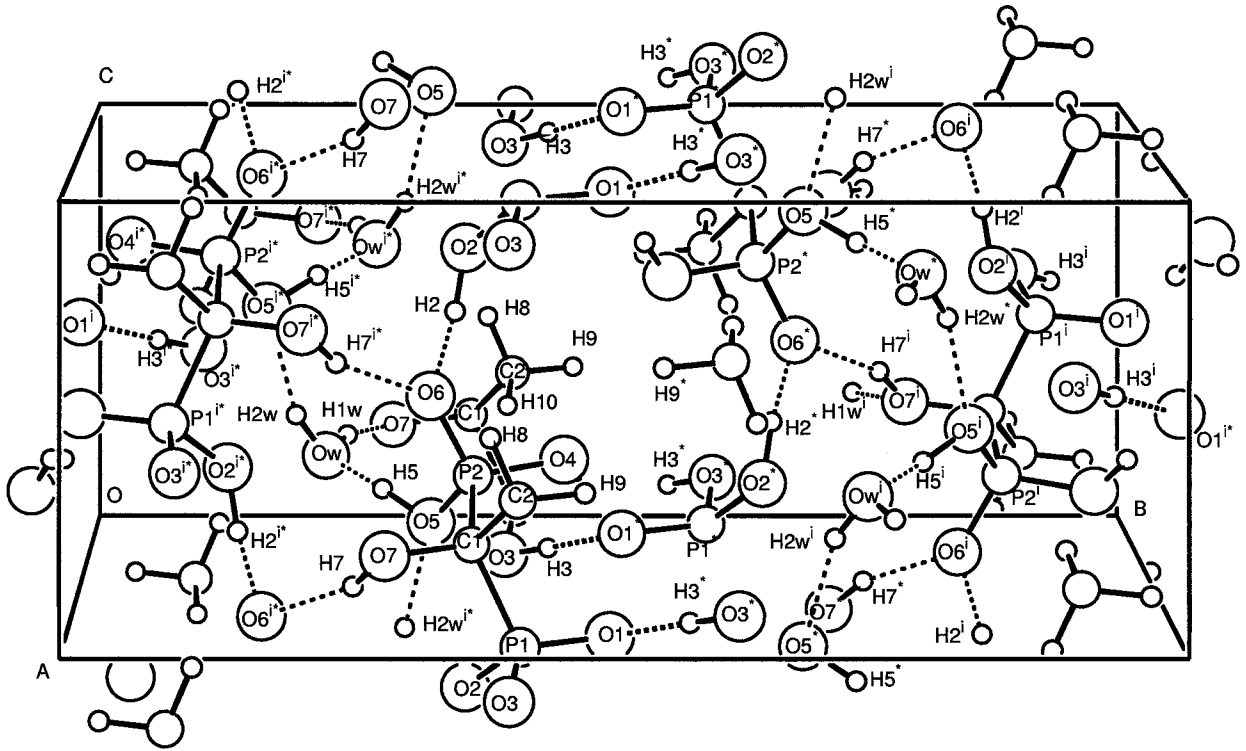

FIGURE 4 General view of the HEBP·H_2O crystal structure (hydrogen bonds in dashed lines). Symmetry code: $^{*}-x, -y, -z$; $^{i}: x, 0.5-y, 0.5+z$; $^{i*}: -x, y-0.5, 0.5-z$.

TABLE VI Principal Atomic Planes in the HEBP Molecules*

P1—C1—P2 plane: $-0.1624x \pm 0.8818y \pm 0.4428z + 7.1296 = 0$			
O3	0.075(1)	O6	0.027(1)
C2—C1—O7 plane: $0.6572x + 0.2261y \pm 0.7190z - 4.0483 = 0$			
H7	0.057(3)	H9	0.055(4)
H8	−0.884(4)	H10	0.860(4)
O1—P1—O2 plane: $0.6660x + 0.2084y \pm 0.7262z - 5.4970 = 0$			
H2	0.914(2)		
O4—P2—O5 plane: $0.6760x + 0.2544y \pm 0.6916z - 2.7968 = 0$			
H4	0.233(3)	H5	−0.914(3)

*The shifts of the outplane atoms given are in Å with estimated standard deviations in parenthesis.

CONCLUSION

This work is the second complete structure determination by neutron diffraction concerning the hydroxybisphosphonic compounds and related salts after $Rb(HEBP)\cdot 2H_2O$. The configuration of the HEBP molecule, the hydrogen atom positions, and the lengths of the hydrogen bonds have been precised. By another way the influence of the complexation of a cation on the skeleton of the HEBP molecule is displayed by comparison between $HEBP\cdot H_2O$ and $Rb(HEBP)\cdot 2H_2O$ taken for example.

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