

## Zoledronate complexes. III. Two zoledronate complexes with alkaline earth metals: $[\text{Mg}(\text{C}_5\text{H}_9\text{N}_2\text{O}_7\text{P}_2)_2(\text{H}_2\text{O})_2]$ and $[\text{Ca}(\text{C}_5\text{H}_8\text{N}_2\text{O}_7\text{P}_2)(\text{H}_2\text{O})]_n$

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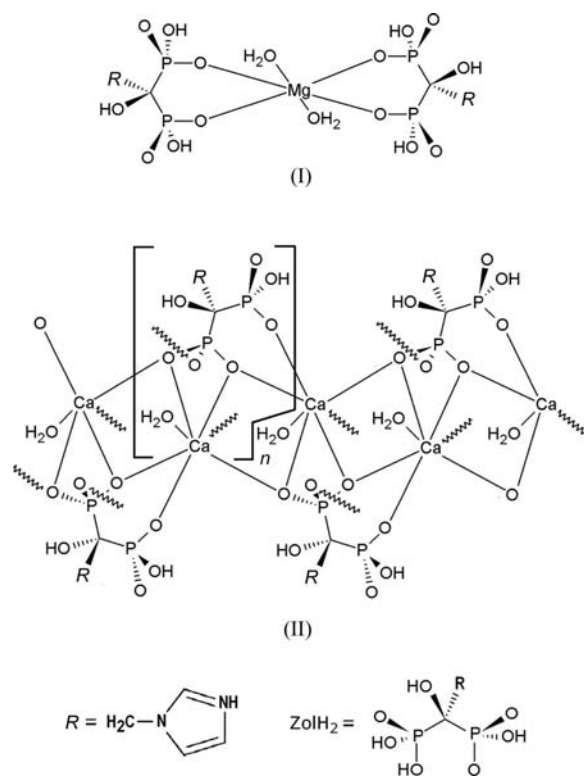
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Diaquabis[dihydrogen 1-hydroxy-2-(imidazol-3-ium-1-yl)ethylidene-1,1-diphosphonato- $\kappa^2 O, O'$ ]magnesium(II),  $[\text{Mg}(\text{C}_5\text{H}_9\text{N}_2\text{O}_7\text{P}_2)_2(\text{H}_2\text{O})_2]$ , consists of isolated dimeric units built up around an inversion centre and tightly interconnected by hydrogen bonding. The  $\text{Mg}^{\text{II}}$  cation resides at the symmetry centre, surrounded in a rather regular octahedral geometry by two chelating zwitterionic zoledronate(1<sup>-</sup>) [or dihydrogen 1-hydroxy-2-(imidazol-3-ium-1-yl)ethylidene-1,1-diphosphonate] anions and two water molecules, in a pattern already found in a few reported isologues where the anion is bound to transition metals (Co, Zn and Ni). *catena*-Poly[[aqua-calcium(II)]- $\mu_3$ -[hydrogen 1-hydroxy-2-(imidazol-3-ium-1-yl)ethylidene-1,1-diphosphonato]- $\kappa^5 O:O, O':O', O''$ ],  $[\text{Ca}(\text{C}_5\text{H}_8\text{N}_2\text{O}_7\text{P}_2)(\text{H}_2\text{O})]_n$ , consists instead of a  $\text{Ca}^{\text{II}}$  cation in a general position, a zwitterionic zoledronate(2<sup>-</sup>) anion and a coordinated water molecule. The geometry around the  $\text{Ca}^{\text{II}}$  atom, provided by six bisphosphonate O atoms and one water ligand, is that of a pentagonal bipyramid with the  $\text{Ca}^{\text{II}}$  atom displaced by 0.19 Å out of the equatorial plane. These  $\text{Ca}^{\text{II}}$  coordination polyhedra are 'threaded' by the  $2_1$  axis so that successive polyhedra share edges of their pentagonal basal planes. This results in a strongly coupled rhomboidal  $\text{Ca}_2\text{-O}_2$  chain which runs along [010]. These chains are in turn linked by an apical O atom from a  $-\text{PO}_3$  group in a neighbouring chain. This O-atom, shared between chains, generates strong covalently bonded planar arrays parallel to (100). Finally, these sheets are linked by hydrogen bonds into a three-dimensional structure. Owing to the extreme affinity of zoledronic acid for bone tissue, in general, and with calcium as one of the major constituents of bone, it is expected that this

structure will be useful in modelling some of the biologically interesting processes in which the drug takes part.

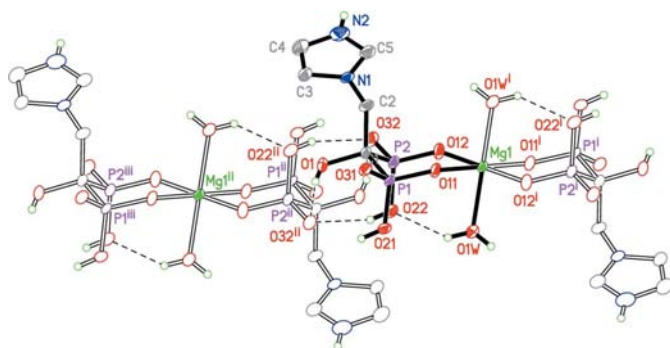
### Comment

Bisphosphonates (BPs) are an important class of osteotropic compounds that are effective in treating benign and malignant skeletal diseases characterized by enhanced osteoclast-mediated bone resorption (osteoporosis, Paget's disease and tumour-induced osteolysis; see, for instance, Green, 2005). BPs in general and zoledronic acid in particular act as a bone 'shield' incorporated into the skeleton, achieving therapeutic concentrations and thus inhibiting bone resorption by cellular effects on osteoclasts. As part of a programme of research on monovalent and divalent alkaline cation complexes with the zoledronate anion (hereafter Zol), we have recently reported the first two structures of this type, namely  $[\text{K}(\text{Zol}^-)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ , (III) (Freire *et al.*, 2010*a*), where all constituents (cation:anion:water<sub>coord</sub>:water<sub>solv</sub>, where water<sub>coord</sub> and water<sub>solv</sub> are coordinated and solvent water molecules, respectively) appeared in a rather simple 1:1:1:1 ratio, and  $[\text{Na}_3(\text{Zol}^{0.5-})_2(\text{Zol}^-)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ , (IV) (Freire *et al.*, 2010*b*), with a more complex 3:4:4:2 component ratio. A thorough introduction to zoledronate complexes has been included in the first of these reports, to which the interested reader is referred.

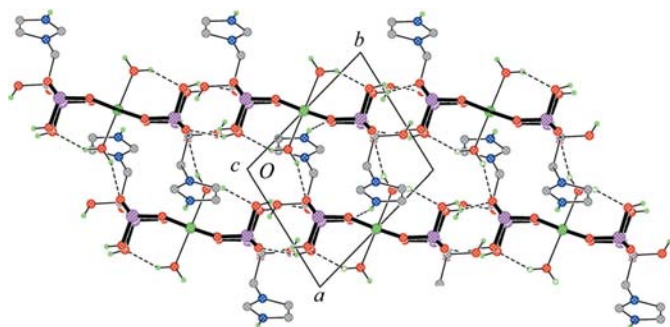


As a continuation of this series, we present herein the structures of two new zoledronate complexes, this time with divalent alkaline cations, *viz.*  $[\text{Mg}(\text{Zol}^-)_2(\text{H}_2\text{O})_2]$ , (I), and  $[\text{Ca}(\text{Zol}^{2-})(\text{H}_2\text{O})]_n$ , (II), the latter being a structure with indubitable interest from a biological point of view, a fact addressed in the concluding remarks of this paper.

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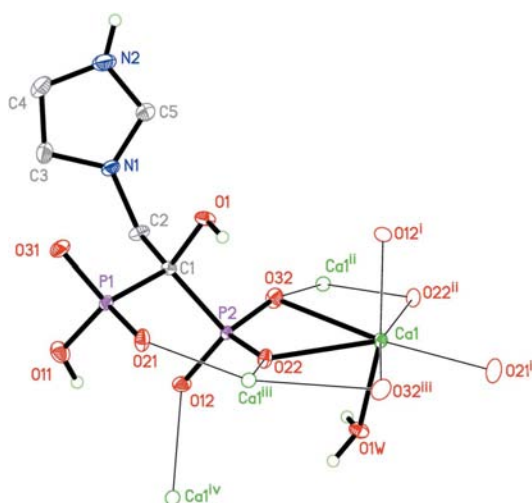
**Figure 1**

A displacement ellipsoid plot (40% probability) of (I), showing (in bold) the asymmetric unit and the symmetry-related part completing the molecule. Intra- and intermolecular interactions defining a hydrogen-bonded chain along [111] are shown as dashed lines. [Symmetry codes: (i)  $-x + 2, -y + 1, -z + 2$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $x - 1, y - 1, z - 1$ .]

**Figure 2**

A packing view of (I) down [001], where the  $(1\bar{1}0)$  planes can be seen (horizontally) in projection. The interconnected molecular cores are drawn in bold, differentiating them from the interplanar connectors, *viz.* the imidazole ring and apical water molecules. Hydrogen bonds are shown as dashed lines.

Compound (I) consists of isolated molecular units built up around an inversion centre (Fig. 1) and tightly interconnected by hydrogen bonding (Fig. 2). The Mg1 cation resides at an inversion centre, surrounded by two chelating  $\text{Zol}^-$  anions and two coordinating water molecules. This 1:2:2:0 cation:anion:water<sub>coord</sub>:water<sub>solv</sub> pattern has already been found in some transition metal zoledronate complexes, the present structure being isomorphous with the Co and Ni (Cao *et al.*, 2007) and Zn (Freire & Vega, 2009) isologues, so that only a very brief discussion will be included here. The rather regular octahedron built up around the cation presents an Mg—O range of 2.0389 (16)–2.1132 (17) Å and a (*cis*)O—Mg1—O angular range of  $90 \pm 4.13$  (8)°. Each zoledronate ligand displays its usual zwitterionic character, with a protonated imidazole ring and two singly protonated phosphonate groups, with a resulting overall  $-1$  total charge. This arrangement provides charge balance. P—OH distances [mean = 1.575 (5) Å] are, as expected, significantly longer than the P—O distances [mean = 1.504 (5) Å], in agreement with the findings for related structures (*e.g.* Coiro *et al.*, 1989; Vega *et al.*, 1996, 1998). The phosphonate groups present an ‘eclipsed’ conformation when viewed along the P1···P2 direction (very nearly along the *c* axis), with an almost perfect O31—P1—

**Figure 3**

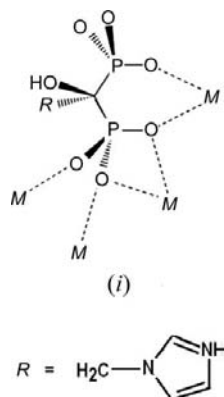
A displacement ellipsoid plot (40% probability) of (II), showing (in bold) the asymmetric unit and the symmetry-related part completing the coordination polyhedron. [Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .]

C1—P2—O32 planar disposition (mean deviation from the plane = 0.012 Å).

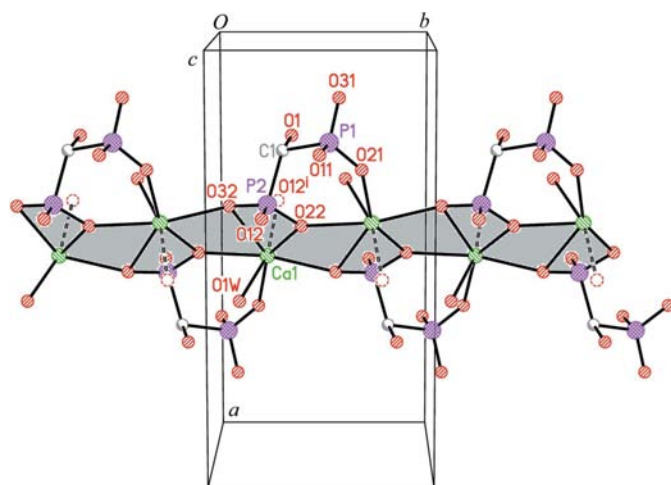
The molecules interact actively through hydrogen bonding, with all available O—H and N—H groups taking part. The hydrogen bond involving O1W—H1WB (Table 1) is intramolecular and provides cohesion to the molecule; those involving O1—H1O and O22—H22O link molecules together in a head-to-tail fashion (Fig. 2), defining chains parallel to [111]. The hydrogen bond involving O21—H21O links chains laterally to form planar arrays parallel to  $(1\bar{1}0)$ , which are finally connected with their upper/lower neighbours *via* the remaining hydrogen bonds involving N2—H2N and O1W—H1WA (Table 1). The interconnected dimeric cores are drawn in bold, differentiating them from the interplanar connectors, *viz.* the imidazole ring and apical water molecules.

Compound (II) is much more interesting in its structural features; it consists of a  $\text{Ca}^{\text{II}}$  cation, a zwitterionic  $\text{Zol}^{2-}$  anion with a single H atom on just one of its phosphonate groups and the usual protonated imidazole ring (thus providing the required two negative charges for charge balance) and a coordinated water molecule (Fig. 3). This rather simple 1:1:1:0 cation:anion:water<sub>coord</sub>:water<sub>solv</sub> formulation expands into a tight two-dimensional network due to the coordination of the Ca1 cation by six ligating O atoms belonging to four different symmetry-related zoledronate units; there is, in addition, a seventh bond to a water ligand. This represents a new  $\mu_4:\kappa^4$  binding mode for the  $\text{Zol}^{2-}$  anion, shown schematically in Fig. 4 and labelled as ‘(i)’, which should be considered an additional binding mode to those presented in Freire *et al.* (2010a,b).

It is perhaps worth mentioning that the present coordination mode, as well as the one labelled ‘(f)’ in the potassium complex reported in Freire *et al.* (2010a), display an unusual  $\mu_1:\kappa^2$  bidentate mode for one of the individual phosphonates, a rather unusual behaviour for this family of ligands, predicted as ‘unfavourable’ by some pioneering calculations using mol-



**Figure 4**  
The new  $\mu_4:\kappa^4$  coordination mode displayed by zoledronate in (II). This should be considered an additional binding mode to those shown in both Figs. 2 in Freire *et al.* (2010a,b).

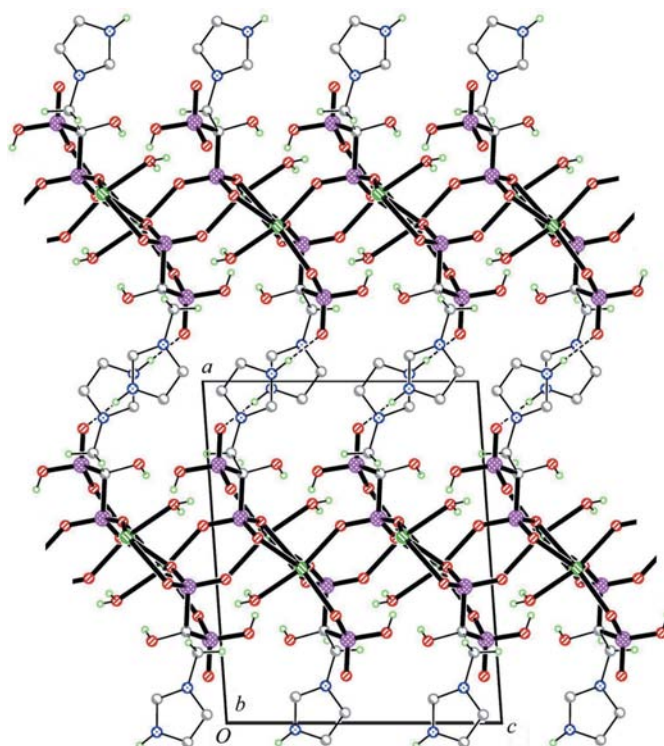


**Figure 5**  
Schematic representation of a chain in (II), with the imidazole groups removed for clarity. The dashed lines represent Ca—O bonds, linking chains laterally, to form two-dimensional structures. [Symmetry code: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .]

ecular electrostatic potentials (Björkroth *et al.*, 1992) and confirmed as such by the very few examples which can be found in the literature, not only for zoledronate but for bisphosphonates in general as well.

There are four other reported seven-coordinated Ca bisphosphonates in the literature, one in Kontturi *et al.* (2002) and three in Kontturi *et al.* (2004); in all of them only four O atoms arising from bisphosphonate units are involved in the metal coordination, while the remaining three sites are occupied by water molecules. As expected, the result is a more open structure than that found in (II), as shown by the calculated densities [1.758, 1.918, 1.947 and 2.042 Mg m<sup>-3</sup>, respectively, against 2.058 Mg m<sup>-3</sup> for (II)].

In compound (II) the geometry around Ca1 is pentagonal bipyramidal; the basal pentagon is essentially planar (mean deviation = 0.13 Å), but with the calcium displaced from this mean plane by 0.19 Å. Six of the Ca—O bonds in the polyhedron have similar lengths in the range 2.3386 (17)–



**Figure 6**  
Packing diagram of (II), viewed along [010], showing the planes in projection. The Ca bisphosphonate structure is emphasized in bold and dashed lines show the imidazole groups connecting the two-dimensional structures *via* the N—H...O bond.

2.4393 (18) Å (Table 2), but the seventh bond, a basal bond, is much longer [Ca1—O32 = 2.7605 (19) Å].

The bisphosphonate ligand in (II) differs from that in (I) in that only one of the phosphonate units carries an H atom and, as in (I), the P—OH distance is significantly longer than the remaining P—O distances [P1—O11 = 1.5915 (19) Å *versus* 1.4919 (17) and 1.4993 (18) Å for the others]. The second phosphonate unit, containing no H atom, shows a much more even distribution of P—O distances, in the range 1.5174 (17)–1.5311 (19) Å, thus indicating marked delocalization of the negative charges. The overall geometry of the anion resembles that of (I), with an eclipsed setting of both phosphonate groups and a very planar disposition of the O31—P1—C1—P2—O32 group (mean deviation from the best plane = 0.011 Å).

Regarding coordination, the bisphosphonate groups act in a rather asymmetric fashion: five of the six PO<sub>3</sub> oxygens which bind the cation pertain to the same phosphonate unit (P2), distributed among four different symmetry-related zoledronate moieties (Table 2). These Ca coordination polyhedra are ‘threaded’ by the 2<sub>1</sub> axis passing within 0.97 Å of atom Ca1, so that  $b/2$  translations of the polyhedra result in their juxtaposition with each other and the sharing of an edge of their pentagonal basal planes. This is mainly the result of atoms O22 and O32 acting in a  $\mu_2$  chelating–bridging mode which determines a chain of Ca<sub>2</sub>O<sub>2</sub> links evolving along [010]. O21, the only basal oxygen not directly involved in the short

bridges subtended by O22 and O32, takes part in a long O—P—C—P—O bridge joining neighbouring cations in the chain (Fig. 5). The result is a rhomboidal Ca<sub>2</sub>—O<sub>2</sub> sequence, with a medium-length Ca···Ca separation of 4.023 (1) Å along [010].

The two apical O atoms fulfil quite different roles: O1W is involved in hydrogen bonding (Table 3), while O12 at (*x*,  $-y + \frac{1}{2}$ ,  $z - \frac{1}{2}$ ) is part of a phosphonate group in a neighbouring chain, thus providing a covalent link along [001] between chains. This defines strongly coupled two-dimensional covalent structures parallel to (100), represented in bold in Fig. 6, where the chains shown in Fig. 5 are shown side-on, as short oblique motifs, interlinked by the P—O—Ca bridges into two-dimensional layers. All the hydrogen bonds presented in Table 3 take place in this zone and are, in this sense, 'inter-layer', with the exception of that involving N2—H2N, which serves to connect these broad planes into a three-dimensional structure. These interactions are also shown in Fig. 6.

As already noted above, zoledronic acid acts as a bone 'shield' incorporated into the skeleton; the way it does so is apparently by complexing the Ca cations in the bones, and in this respect the structure described here shows clear evidence of the avidity of zoledronate oxygens for the Ca cations. This is the reason why this latter Ca zoledronate complex is by far the most interesting of all the complexes of the anion reported so far, and it is expected that this structure will be useful in modelling some of the biologically interesting processes in which the drug takes part.

## Experimental

Crystals of (I) and (II) were synthesized from a solution of zoledronic acid (from Gador Argentina S.A.) with a metal salt solution in a 2:1 stoichiometric ratio, using Mg(NO<sub>3</sub>)<sub>2</sub> for (I) and CaCl<sub>2</sub> for (II). Crystals of (I) were grown at 353 K; the unperturbed solution was allowed to concentrate slowly and after a few days, large colourless blocks were obtained which were suitable for single-crystal X-ray diffraction. Crystals of (II) were grown in a 45 ml Teflon-lined autoclave under hydrothermal conditions over a few days at 400 K.

### Compound (I)

#### Crystal data

[Mg(C <sub>5</sub> H <sub>9</sub> N <sub>2</sub> O <sub>7</sub> P <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <i>M<sub>r</sub></i> = 602.51 Triclinic, <i>P</i> $\bar{1}$ <i>a</i> = 7.4680 (15) Å <i>b</i> = 8.4390 (17) Å <i>c</i> = 9.819 (2) Å $\alpha$ = 105.11 (3)° $\beta$ = 111.98 (3)°	$\gamma$ = 97.04 (3)° <i>V</i> = 537.0 (3) Å <sup>3</sup> <i>Z</i> = 1 Mo <i>K</i> α radiation $\mu$ = 0.47 mm <sup>-1</sup> <i>T</i> = 294 K 0.28 × 0.22 × 0.20 mm
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#### Data collection

Rigaku AFC6 diffractometer Absorption correction: $\psi$ scan (North <i>et al.</i> , 1968) <i>T</i> <sub>min</sub> = 0.78, <i>T</i> <sub>max</sub> = 0.83 2554 measured reflections 2103 independent reflections	1875 reflections with <i>I</i> > 2σ( <i>I</i> ) <i>R</i> <sub>int</sub> = 0.037 3 standard reflections every 150 reflections intensity decay: 1%
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**Table 1**  
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1O···O32 <sup>i</sup>	0.85	2.06	2.904 (2)	170
O1W—H1WA···O31 <sup>ii</sup>	0.85	1.94	2.744 (2)	158
O1W—H1WB···O22	0.85	2.41	3.124 (3)	142
O21—H21O···O31 <sup>iii</sup>	0.85	1.76	2.600 (2)	169
O22—H22O···O32 <sup>i</sup>	0.85	1.93	2.667 (3)	145
N2—H2N···O12 <sup>iv</sup>	0.84	1.93	2.741 (3)	161

Symmetry codes: (i)  $-x + 1, -y, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x + 1, -y, -z + 2$ ; (iv)  $-x + 1, -y + 1, -z + 1$ .

**Table 2**  
Selected bond lengths (Å) for (II).

Ca1—O12 <sup>i</sup>	2.3386 (17)	Ca1—O22	2.4338 (18)
Ca1—O22 <sup>ii</sup>	2.3637 (18)	Ca1—O1W	2.4393 (18)
Ca1—O21 <sup>iii</sup>	2.3655 (17)	Ca1—O32	2.7605 (19)
Ca1—O32 <sup>iii</sup>	2.3902 (18)		

Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

**Table 3**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2N···O31 <sup>iv</sup>	0.88	1.72	2.590 (3)	168
O1W—H1WB···O12 <sup>v</sup>	0.85	1.88	2.722 (3)	173
O1W—H1WA···O21 <sup>vi</sup>	0.85	1.93	2.773 (3)	170
O1—H1O···O1W <sup>iii</sup>	0.85	1.97	2.786 (2)	161
O11—H11O···O32 <sup>vii</sup>	0.85	2.41	3.066 (3)	135
O11—H11O···O12	0.85	2.40	3.017 (2)	130

Symmetry codes: (iii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $-x + 1, -y, -z + 1$ ; (vi)  $-x + 1, -y + 1, -z + 1$ ; (vii)  $x, -y + \frac{1}{2}, z + \frac{1}{2}$ .

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$ $wR(F^2) = 0.151$ <i>S</i> = 0.96 2103 reflections	165 parameters H-atom parameters constrained $\Delta\rho_{\max} = 0.93 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.94 \text{ e } \text{Å}^{-3}$
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### Compound (II)

#### Crystal data

[Ca(C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> O <sub>7</sub> P <sub>2</sub> )(H <sub>2</sub> O)] <i>M<sub>r</sub></i> = 328.17 Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i> <i>a</i> = 13.7027 (15) Å <i>b</i> = 7.0429 (8) Å <i>c</i> = 11.0040 (12) Å $\beta$ = 94.007 (10)°	<i>V</i> = 1059.4 (2) Å <sup>3</sup> <i>Z</i> = 4 Mo <i>K</i> α radiation $\mu$ = 0.93 mm <sup>-1</sup> <i>T</i> = 294 K 0.32 × 0.10 × 0.06 mm
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#### Data collection

Oxford Diffraction Gemini CCD S Ultra diffractometer Absorption correction: multi-scan ( <i>CrysAlis Pro</i> ; Oxford Diffraction, 2009) <i>T</i> <sub>min</sub> = 0.78, <i>T</i> <sub>max</sub> = 0.88	4725 measured reflections 2384 independent reflections 1798 reflections with <i>I</i> > 2σ( <i>I</i> ) <i>R</i> <sub>int</sub> = 0.029
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#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.085$ <i>S</i> = 0.96 2384 reflections	168 parameters H-atom parameters constrained $\Delta\rho_{\max} = 0.61 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.62 \text{ e } \text{Å}^{-3}$
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H atoms attached to O and N atoms were found in a difference Fourier map, further idealized ( $O-H = 0.85 \text{ \AA}$ ,  $H \cdots H = 1.35 \text{ \AA}$  and  $N-H = 0.87 \text{ \AA}$ ) and finally allowed to ride (see the discussion below about the  $O1-H1O$  pair). H atoms attached to C atoms were placed at calculated positions ( $C-H = 0.93$  and  $0.97 \text{ \AA}$  for CH and  $CH_2$  groups, respectively) and allowed to ride. Isotropic displacement parameters were refined freely for all water and hydroxy H atoms in both structures and for the  $N-H$  H atom of (II). For all other H atoms, the  $U_{iso}(H)$  value was set at  $U_{eq}(\text{host atom})$ .

The final difference maps for (I) showed some interesting features. The first concerns the behaviour of the refinement algorithm as applied to the P atoms. In spite of the refinement of (I) being carried out without any restraints or constraints, the least-squares procedure seemingly failed to provide an adequate anisotropic treatment for atoms P1 and P2; in the final difference maps, both atoms appeared flanked by pairs of (opposite) positive and negative electron-density peaks of *ca*  $1 \text{ e \AA}^{-3}$  in height (at  $0.85-0.95 \text{ \AA}$  from phosphorus), in a 'crossed' arrangement typical of an insufficient anisotropic modelling of the displacement ellipsoids of both atoms. The second is the clear evidence of an (asymmetric) splitting in the  $O1-H1O \cdots O32(1-x, -y, 1-z)$  hydrogen bond, with a H-atom transfer from O1 towards O32 of the order of 10–15%, both sites displaying equilibrium positions with similar O–H distances ( $0.80-0.90 \text{ \AA}$ ), as displayed by the difference map. Owing to the very low occupancy, this disorder has not been included in the model, where atom H1O was assigned unit site occupancy.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988) for (I); *CrysAlis Pro* (Oxford Diffraction, 2009) for (II). Cell refinement: *MSC/AFC Diffractometer Control Software* for (I); *CrysAlis Pro* for (II). Data reduction: *MSC/AFC Diffractometer Control Software* for (I); *CrysAlis Pro* for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008). Molecular graphics: *SHELXTL* (Sheldrick, 2008) for (I); *ORTEP-3 for Windows* (Farrugia, 1997) for (II). Software used to prepare material for

publication: *SHELXTL* and *PLATON* (Spek, 2009) for (I); *SHELXL97* and *PLATON* for (II).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3341). Services for accessing these data are described at the back of the journal.

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