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Crystal structure of *catena*-poly[[tetraaqua-magnesium]-μ-(dihydrogen hypodiphosphato)-$\kappa^2O:O'$]

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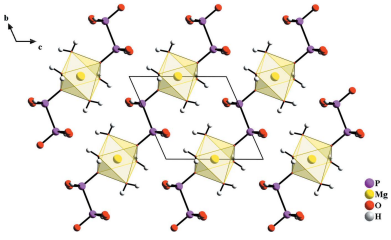
The crystal structure of the title compound, $[Mg(H_2P_2O_6)(H_2O)_4]_n$, is built up from $(H_2P_2O_6)^{2-}$ anions bridging Mg^{2+} cations into chains extending parallel to [011]. The Mg^{2+} ion is located on an inversion centre and is octahedrally coordinated by the O atoms of two $(H_2P_2O_6)^{2-}$ anions and four water molecules. The centrosymmetric $(H_2P_2O_6)^{2-}$ anion has a staggered conformation whereby the tetravalent phosphorus atom is surrounded tetrahedrally by three O atoms and by one symmetry-related P atom. A three-dimensional O—H···O hydrogen-bonded network of medium strength involving the P—OH group of the anion and the water molecules is present.

1. Chemical context

A considerable number of alkaline metal hypodiphosphates have been characterized in the last few years (Szafranowska *et al.*, 2012; Wu *et al.*, 2012; Gjikaj *et al.*, 2012, 2014). Until today, the described alkaline metal hypodiphosphates have only been of academic interest, with the exception of ammonium and sodium dihydrogenhypodiphosphates (Collin & Willis, 1971). The acidic solutions of sodium dihydrogenhypodiphosphate are used for the gravimetric immobilization of uranium(IV) as $U_2P_2O_6{\cdot}3H_2O$ and UP_2O_7 (Bloss *et al.*, 1967). Furthermore, ammonium dihydrogenhypodiphosphate finds a use as a flame retardant (Ruflin *et al.*, 2007), and its ferroelectricity has recently been discovered (Szklarz *et al.*, 2011).

The alkaline earth metal hypodiphosphates were first described by Salzer (1878). $Ca_2P_2O_6{\cdot}2H_2O$ and $BaH_2P_2O_6{\cdot}2H_2O$ were first synthesized by Palmer (1961), but structural data of hypodiphosphates of the alkaline earth metals are still missing. Here, we report the synthesis and the crystal structure of $[Mg(H_2P_2O_6)(H_2O)_4]$.



2. Structural commentary

The principal building units in the crystal structure of $[Mg(H_2P_2O_6)(H_2O)_4]$ are $[MgO_6]$ octahedra and $(H_2P_2O_6)^{2-}$ anions, forming chains extending parallel to [011] (Fig. 1). In the chains, each Mg^{2+} cation is bridged by two anions (Fig. 2). The Mg^{2+} ion is located on an inversion centre and is octahedrally coordinated by two $(H_2P_2O_6)^{2-}$ anions and by four water molecules with Mg—O bond lengths ranging from 2.0580 (17) to 2.0646 (18) Å. In the $(H_2P_2O_6)^{2-}$ anion, which is located about an inversion centre and has a staggered conformation, the tetravalent P atom is surrounded by three O atoms and one symmetry-related P atom with a P—P distance

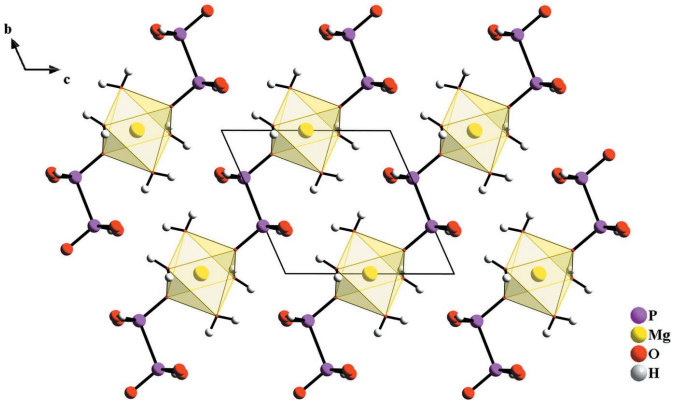


Figure 1
The crystal structure of the title compound, viewed along [100], showing the chain architecture.

of 2.1843 (12) Å and P—O distances ranging from 1.5013 (16) to 1.5855 (16) Å. All bond lengths and angles of the hypodiphosphate anion are well within the expected ranges (Szafranowska *et al.*, 2012; Gjikaj *et al.*, 2014) and are comparable to those found for $M_2P_2O_6{\cdot}12H_2O$ (M = Co and Ni; Hagen & Jansen, 1995; Haag *et al.*, 2005).

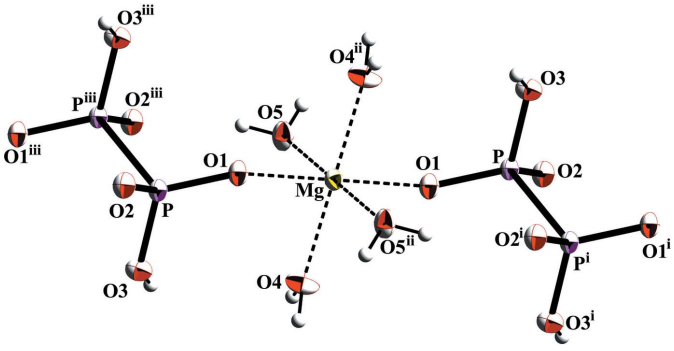


Figure 2
The molecular entities in the title compound with atom labels and displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x, -y+2, -z+1$; (iii) $x, y+1, z+1$.]

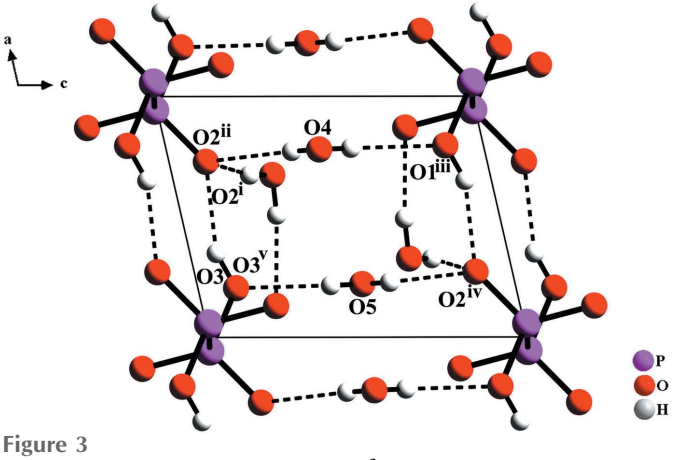


Figure 3
The hydrogen bonds between $(H_2P_2O_6)^{2-}$ anions and water molecules in the title compound. The symmetry codes are as in Table 1.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2^{i}	0.79 (4)	1.94 (4)	2.687 (2)	157 (3)
O4—H4A···O2^{ii}	0.82 (3)	2.00 (3)	2.817 (2)	169 (3)
O4—H4B···O1^{iii}	0.85 (4)	1.94 (4)	2.786 (2)	173 (3)
O5—H5A···O2^{iv}	0.75 (4)	2.03 (4)	2.768 (3)	165 (3)
O5—H5B···O3^{v}	0.77 (4)	2.08 (4)	2.829 (3)	165 (4)

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

3. Supramolecular features

The crystal structure of $[Mg(H_2P_2O_6)(H_2O)_4]$ exhibits a three-dimensional hydrogen-bonded network, in which the $(H_2P_2O_6)^{2-}$ anions are joined into ribbons along [100] by centrosymmetric pairs of PO3—H3···O2 hydrogen bonds (Table 1 and Fig. 3). The O···O distances between the $(H_2P_2O_6)^{2-}$ anions and water molecules located between the ribbons range from 2.786 (3) to 2.829 (3) Å), indicating hydrogen bonds of medium strength (Table 1). These values agree very well with those reported for $Rb_2H_2P_2O_6{\cdot}2H_2O$ (Wu *et al.*, 2012).

4. Synthesis and crystallization

Disodium dihydrogenhypodiphosphate was prepared according to Leininger & Chulski (1953). An aqueous solution

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Mg(H_2P_2O_6)(H_2O)_4]$
M_r	256.33
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	223
a, b, c (Å)	5.1486 (15), 6.595 (2), 7.096 (2)
α, β, γ (°)	112.31 (2), 98.55 (2), 98.28 (2)
V (Å^3)	215.09 (11)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.61
Crystal size (mm)	0.28 × 0.25 × 0.23
Data collection	
Diffractometer	Stoe IPDS-II
Absorption correction	Numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 1999, 2001)
T_{min}, T_{max}	0.843, 0.869
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2193, 799, 739
R_{int}	0.057
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.609
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.15
No. of reflections	799
No. of parameters	81
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.60, −0.53

Computer programs: *X-AREA* (Stoe & Cie, 2002), *SHELXS97* and *SHELXL97* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

of hypodiphosphoric acid was obtained by passing a saturated solution of disodium dihydrogenhypodiphosphate through a cation-exchange resin (Dowex 50WX2 50–100). About 40 ml of an aqueous solution of hypodiphosphoric acid ($H_4P_2O_6$) were collected in the pH range 1.5–3.5 and subsequently added to magnesium carbonate (117 mg) at room temperature. Colourless block-shaped crystals of the title compound were obtained after several days at 278 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in a difference Fourier map and were refined isotropically without restraints.

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Crystal structure of *catena*-poly[[tetraaquamagnesium]-μ-(dihydrogen hypodiphosphato)-κ^2O:O']

Mimoza Gjikaj and Madeline Haase

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2012); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

catena-Poly[[tetraaquamagnesium]-μ-(dihydrogen hypodiphosphato)-κ^2O:O']

Crystal data

$[Mg(H_2P_2O_6)(H_2O)_4]$
$M_r = 256.33$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.1486$ (15) Å
$b = 6.595$ (2) Å
$c = 7.096$ (2) Å
$\alpha = 112.31$ (2)°
$\beta = 98.55$ (2)°
$\gamma = 98.28$ (2)°
$V = 215.09$ (11) Å^3
$Z = 1$
$F(000) = 132$
$D_x = 1.979$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3841 reflections
$\theta = 3.2$–25.7°
$\mu = 0.61$ mm^{-1}
$T = 223$ K
Block-shaped, colourless
0.28 × 0.25 × 0.23 mm

Data collection

Stoe IPDS-II diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–scans
Absorption correction: numerical (*X-SHAPE* and *X-RED*; Stoe & Cie, 1999, 2001)
$T_{min} = 0.843$, $T_{max} = 0.869$
2193 measured reflections
799 independent reflections
739 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.7°$, $\theta_{min} = 3.2°$
$h = -6\rightarrow6$
$k = -8\rightarrow8$
$l = -8\rightarrow8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.15$
799 reflections
81 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0594P)^2 + 0.0577P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
P	0.05636 (10)	0.66957 (9)	0.00780 (8)	0.0119 (2)
Mg	0.0000	1.0000	0.5000	0.0118 (3)
O1	0.1302 (3)	0.8332 (3)	0.2329 (2)	0.0158 (4)
O2	0.2710 (3)	0.6732 (3)	−0.1158 (2)	0.0167 (4)
O3	−0.2044 (3)	0.6995 (3)	−0.1200 (2)	0.0180 (4)
O4	0.3263 (3)	0.9689 (3)	0.6850 (3)	0.0233 (4)
O5	0.2204 (3)	1.2973 (3)	0.5191 (3)	0.0207 (4)
H3	−0.345 (8)	0.697 (6)	−0.086 (6)	0.041 (9)*
H4A	0.326 (6)	0.895 (5)	0.756 (5)	0.019 (7)*
H4B	0.491 (7)	1.027 (5)	0.699 (5)	0.024 (7)*
H5A	0.229 (6)	1.410 (6)	0.605 (6)	0.026 (8)*
H5B	0.220 (7)	1.323 (6)	0.422 (6)	0.041 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0114 (3)	0.0134 (4)	0.0117 (4)	0.0031 (2)	0.0061 (2)	0.0046 (2)
Mg	0.0107 (5)	0.0141 (6)	0.0101 (5)	0.0033 (4)	0.0042 (4)	0.0035 (4)
O1	0.0155 (8)	0.0170 (8)	0.0141 (8)	0.0036 (6)	0.0072 (6)	0.0041 (6)
O2	0.0152 (8)	0.0201 (8)	0.0171 (8)	0.0049 (6)	0.0096 (6)	0.0075 (6)
O3	0.0137 (8)	0.0277 (9)	0.0188 (8)	0.0081 (7)	0.0082 (6)	0.0131 (7)
O4	0.0128 (9)	0.0347 (10)	0.0299 (10)	0.0040 (7)	0.0037 (7)	0.0219 (9)
O5	0.0295 (9)	0.0169 (9)	0.0150 (8)	0.0016 (7)	0.0097 (7)	0.0052 (8)

Geometric parameters (Å, º)

P—O1	1.5013 (16)	Mg—O5^{ii}	2.0646 (18)
P—O2	1.5122 (15)	Mg—O5	2.0646 (18)
P—O3	1.5855 (16)	O3—H3	0.79 (4)
P—P^{i}	2.1843 (12)	O4—H4A	0.82 (3)
Mg—O4^{ii}	2.0580 (17)	O4—H4B	0.85 (4)
Mg—O4	2.0580 (17)	O5—H5A	0.75 (4)

Mg—O1	2.0637 (15)	O5—H5B	0.77 (4)
Mg—O1^{ii}	2.0637 (15)		
O1—P—O2	116.02 (9)	O1^{ii}—Mg—O5^{ii}	88.52 (7)
O1—P—O3	112.90 (9)	O4^{ii}—Mg—O5	90.25 (8)
O2—P—O3	106.05 (9)	O4—Mg—O5	89.75 (8)
O1—P—P^{i}	108.73 (7)	O1—Mg—O5	88.52 (7)
O2—P—P^{i}	108.36 (7)	O1^{ii}—Mg—O5	91.48 (7)
O3—P—P^{i}	104.04 (7)	O5^{ii}—Mg—O5	180.0
O4^{ii}—Mg—O4	180.0	P—O1—Mg	147.48 (9)
O4^{ii}—Mg—O1	88.56 (7)	P—O3—H3	123 (2)
O4—Mg—O1	91.44 (7)	Mg—O4—H4A	128 (2)
O4^{ii}—Mg—O1^{ii}	91.44 (7)	Mg—O4—H4B	125.9 (19)
O4—Mg—O1^{ii}	88.56 (7)	H4A—O4—H4B	106 (3)
O1—Mg—O1^{ii}	180.00 (7)	Mg—O5—H5A	124 (3)
O4^{ii}—Mg—O5^{ii}	89.75 (8)	Mg—O5—H5B	121 (3)
O4—Mg—O5^{ii}	90.25 (8)	H5A—O5—H5B	104 (4)
O1—Mg—O5^{ii}	91.48 (7)		

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{iii}	0.79 (4)	1.94 (4)	2.687 (2)	157 (3)
O4—H4*A*···O2^{iv}	0.82 (3)	2.00 (3)	2.817 (2)	169 (3)
O4—H4*B*···O1^{v}	0.85 (4)	1.94 (4)	2.786 (2)	173 (3)
O5—H5*A*···O2^{vi}	0.75 (4)	2.03 (4)	2.768 (3)	165 (3)
O5—H5*B*···O3^{vii}	0.77 (4)	2.08 (4)	2.829 (3)	165 (4)

Symmetry codes: (iii) *x*−1, *y*, *z*; (iv) *x*, *y*, *z*+1; (v) −*x*+1, −*y*+2, −*z*+1; (vi) *x*, *y*+1, *z*+1; (vii) −*x*, −*y*+2, −*z*.