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Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{P-O}) = 0.002\text{ \AA}$

R factor = 0.021

w R factor = 0.048

Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

A new polymorph of hexaaqua-magnesium(II) bis(hypophosphite)

In a new polymorph of hexaaquamagnesium(II) bis(hypophosphite), $[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$, the planes of *trans* water molecules forming the octahedral coordination sphere of the Mg atoms are in a staggered conformation. The magnesium(II) cations are in a pseudo-face-centered cubic arrangement, with $a \simeq 10.294\text{ \AA}$ and tetrahedral cavities are occupied by P atoms. Hypophosphite anions are hydrogen bonded to the coordinated water molecules.

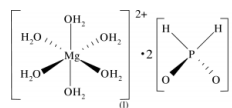
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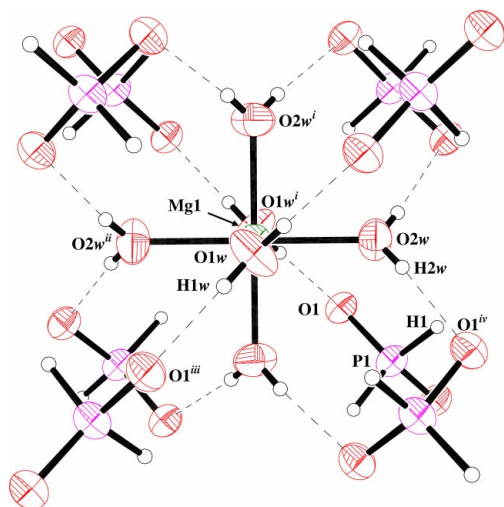
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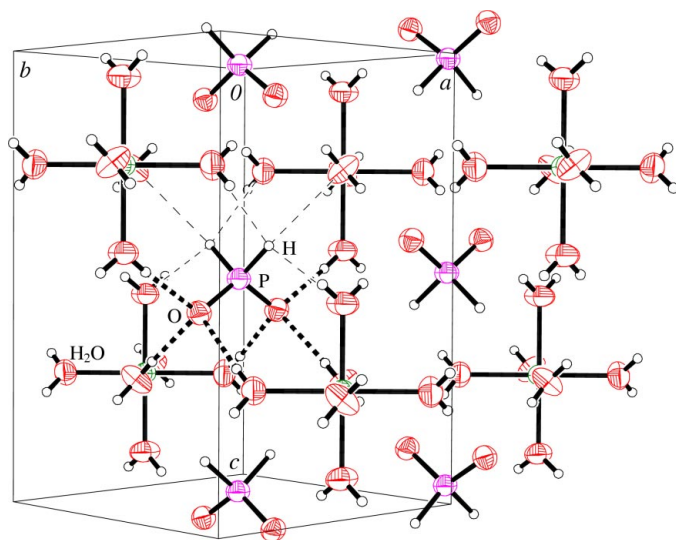
Studies of hexaaquametal(II) bis(hypophosphites) have been reported earlier (Ferrari & Colla, 1937; Pédrázuela *et al.*, 1953; Galigné & Dumas, 1973; Kuratieva *et al.*, 2002, 2003). The structure of a new polymorph, (I), of $[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ is described here; this is different from that previously reported (Galigné & Dumas, 1973) but similar to that of $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$ (Marsh, 1991), excluding the H atoms present in the hypophosphite anion. The packing of the Mg^{II} cations, P and O atoms of hypophosphite anions is the same as in the structure of $[\text{Ni}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ and Cl and O atoms in $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$. The magnesium cations are in a pseudo-face-centered cubic arrangement, with $a \simeq 10.294\text{ \AA}$ (10.371 \AA in $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$) and tetrahedral cavities are occupied by P atoms.



The first coordination sphere of the Mg^{II} cation consists of six water molecules forming a slightly distorted octahedron and appearing in only one type of orientation. Planes of *trans*-coordinated water molecules are in a staggered conformation, as in $[\text{Ni}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ (Kuratieva *et al.*, 2003) and $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$ (Marsh, 1991), but different from $[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ (Galigné & Dumas, 1973), $[\text{Co}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$, and $[\text{Co}_{0.5}\text{Ni}_{0.5}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ (Kuratieva *et al.*, 2002), in which a pair of *trans* water molecules is in an eclipsed conformation. The six coordinated water molecules occur in two groups. The two molecules corresponding to the O1W atoms [$\text{Mg}-\text{O}$ 2.042 (3) \AA] have their planes perpendicular to the basal plane formed by the four other molecules and the Mg^{II} cation. The angle between the normal to the planes of these water molecules is 90.0° {as in $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$ }. The four molecules corresponding to the O2W atoms [$\text{Mg}-\text{O}$ 2.060 (2) \AA] have their planes perpendicular to the basal plane; the angle between the normal to the planes of *trans*


Figure 1

The environment of the hexaaquamagnesium(II) cation in relation to the hypophosphite anions. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii [symmetry codes: (i) $y - \frac{1}{2}, 1 - x, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, z$; (iii) $1 - y, \frac{1}{2} + x, \frac{1}{2} - z$; (iv) $\frac{1}{2} - y, x, z - \frac{1}{2}$].


Figure 2

The environment of the hypophosphite anion of $[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ in relation to the hexaaquamagnesium(II) cations, viewed along $[110]$. Thick dashed lines indicate the $\text{O}-\text{H}\cdots\text{O}-\text{P}$ hydrogen bonds and thin dashed lines indicate the $\text{OW}\cdots\text{H}-\text{P}$ contacts. Displacement ellipsoids are plotted at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

coordinated molecules of this type is $83.3(2)^\circ$ [$88.3(3)^\circ$ in $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$].

The second coordination sphere of the Mg^{II} cation consists of eight hypophosphite anions, which are hydrogen bonded to water molecules. Although the packing of Mg^{II} cations and P atoms is similar, the orientation of hypophosphite anions differs from that in $[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ (Galigné & Dumas, 1973), $[\text{Co}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$, and $[\text{Co}_{0.5}\text{Ni}_{0.5}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$

(Kuratieva *et al.*, 2002), and resembles that in $[\text{Ni}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ (Kuratieva *et al.*, 2003) and $[\text{Mg}(\text{H}_2\text{O})_6](\text{ClO}_2)_2$ (Marsh, 1991). The geometry of the hypophosphite anion remains practically the same as in previous structures (Naumov *et al.*, 2001, 2002; Kuratieva *et al.*, 2002, 2003) (Table 1). Each O atom of the hypophosphite anion is hydrogen bonded to three water molecules from different complex cations (Table 2; thick dashed lines in Fig. 2). Each H atom is surrounded by three water molecules from other complex cations; these H atoms are situated directly above the centers of the triangles formed by the O atoms of these three water molecules (thin dashed lines in Fig. 2). The average $\text{P}-\text{H}\cdots\text{O}$ contact is $2.87(2) \text{ \AA}$. The environment of the hypophosphite anion is similar to that found in the other hexaaquametal(II) bis(hypophosphites) listed above.

Experimental

$[\text{Mg}(\text{H}_2\text{O})_6](\text{H}_2\text{PO}_2)_2$ was synthesized by slow evaporation of an aqueous solution of magnesium(II) hypophosphite, prepared by adding a solution of calcium(II) hypophosphite, $\text{Ca}(\text{H}_2\text{PO}_2)_2$, to a solution of magnesium(II) sulfate heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. The reaction mixture was stored at room temperature for one week in air.

Crystal data

$\text{Mg}(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}_2\text{P}$
 $M_r = 262.38$
 Tetragonal, $P4_2/nmc$
 $a = 7.2187(9) \text{ \AA}$
 $c = 10.4639(13) \text{ \AA}$
 $V = 545.27(12) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.598 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 22 reflections
 $\theta = 11.7\text{--}14.9^\circ$
 $\mu = 0.48 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Prism, colorless
 $0.24 \times 0.20 \times 0.16 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 $2\theta/\theta$ scans
 Absorption correction: empirical (CADDAT; Enraf-Nonius, 1989)
 $T_{\text{min}} = 0.904, T_{\text{max}} = 0.925$
 809 measured reflections
 427 independent reflections
 238 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$
 $\theta_{\text{max}} = 29.1^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 9$
 $l = 0 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.048$
 $S = 0.74$
 427 reflections
 33 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0118P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.016(2)

Table 1

Selected geometric parameters ($\text{Å}, ^\circ$).

Mg1—O1W	2.042(3)	P1—O1	1.5088(18)
Mg1—O2W	2.060(2)	P1—H1	1.356(19)
O1W ⁱ —Mg1—O1W	180.0	O2W—Mg1—O2W ⁱⁱ	90.0
O1W—Mg1—O2W	90.0	O1—P1—O1 ^v	116.08(14)
O2W—Mg1—O2W ⁱⁱⁱ	180.0	H1 ^v —P1—H1	105.2(15)

Symmetry codes: (i) $y - \frac{1}{2}, 1 - x, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{3}{2} - y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W\cdots O1^{iii}$	0.81 (2)	1.94 (2)	2.750 (2)	177 (3)
$O2W-H2W\cdots O1^{iv}$	0.762 (14)	2.006 (14)	2.7662 (14)	175 (2)

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

The H atoms were located from a difference electron-density map and refined without constraints.

Data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CD4CA0*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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