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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ (P—O) = 0.001 Å
R factor = 0.022
wR factor = 0.064
Data-to-parameter ratio = 11.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Diammonium tris[hexaaquamagnesium(II)] tetrakis[hydrogenphosphate(III)], (NH₄)₂[Mg(H₂O)₆]₃(HPO₃)₄**

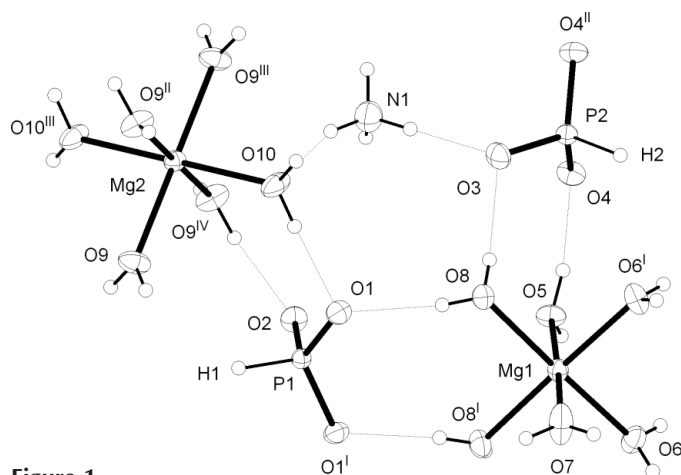
The framework of the title compound is made up of discrete Mg(H₂O)₆ octahedra, and HPO₃ and NH₄ tetrahedra, which are organized in planes parallel to (010). Strong hydrogen bonding between the building units stabilizes the structure. The hydrogenphosphate(III) tetrahedra, the ammonium tetrahedron and one of the two Mg atoms lie on positions with *m* symmetry, whereas the second Mg atom is located on a position with 2/*m* symmetry.

Comment

The work reported in the present paper is a continuation of our investigations focusing on the synthesis of phosphates and phosphites using wet-chemical methods. In the course of this project we have synthesized and structurally characterized various compounds, such as diphosphates (Essehli *et al.*, 2005, and references therein), phosphites (Ouarsal *et al.*, 2003, 2004, and references therein) and monophosphates including (NH₄)CoPO₄·6H₂O (El Bali *et al.*, 2005).

The first structural investigation in the system Mg—P^{III}—O—H was carried out by Corbridge (1956), who determined the crystal structure of MgHPO₃·6H₂O on the basis of two-dimensional X-ray photographic data. This structure was redetermined some years ago (Powell *et al.*, 1994). In the present work, we report the synthesis and crystal structure of the ammonium-containing phase (NH₄)₂Mg₃(HPO₃)₄·18H₂O.

The two independent Mg²⁺ cations lie on positions with 2/*m* (Mg2) and *m* (Mg1) symmetry. They are octahedrally coordinated by six O atoms that all belong to water molecules (Fig. 1). The average Mg—O distance of 2.072 (2) Å is

**Figure 1**

View of the Mg(H₂O)₆, HPO₃ and NH₄ coordination polyhedra. Dashed lines indicate hydrogen bonds; displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) *x*, −*y*, *z*; (ii) *x*, 1 − *y*, *z*; (iii) −*x*, 1 − *y*, −*z*; (iv) −*x*, *y*, −*z*.]

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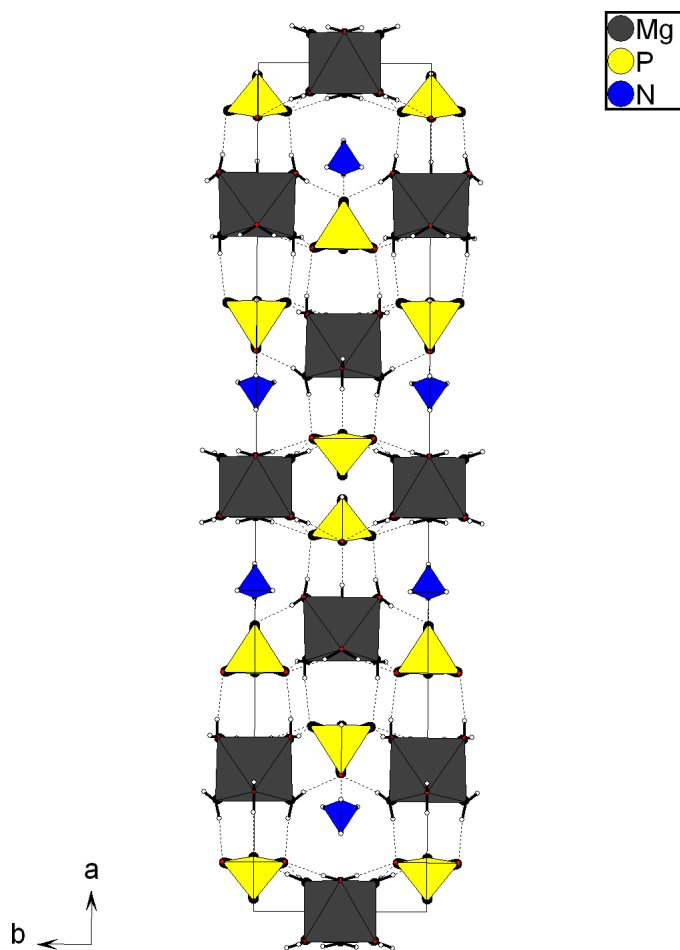


Figure 2
Projection of the crystal structure along *c*. Dashed lines indicate hydrogen bonds.

comparable to that of 2.099 Å reported for $\text{MgHPO}_3 \cdot 6\text{H}_2\text{O}$ (Corbridge, 1956) and to that of 2.086 Å for $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ (Ouarsal *et al.*, 2004). The $\text{Mg}(\text{H}_2\text{O})_6$ octahedra are isolated in the structure, the shortest $\text{Mg} \cdots \text{Mg}$ distance being 6.1666 (3) Å, which is considerably longer than the $\text{Mg} \cdots \text{Mg}$ distance of 5.031 Å found in $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$.

The P atoms occupy two non-equivalent crystallographic positions, both with *m* symmetry. The surrounding tetrahedra consist of three O atoms and one H atom. The average P–H and P–O distances are 1.25 (2) and 1.527 (2) Å, respectively. The distances are in good agreement with those found in $(\text{NH}_4)_2\text{HPO}_3 \cdot \text{H}_2\text{O}$ (1.36 and 1.523 Å; Rafiq *et al.*, 1982) or in $[\text{Zn}_2(\text{H}_2\text{O})_4](\text{HPO}_3)_2 \cdot \text{H}_2\text{O}$ (1.31 and 1.520 Å; Ortiz-Avila *et al.*, 1989).

The crystal structure of $(\text{NH}_4)_2\text{Mg}_3(\text{HPO}_3)_4 \cdot 18\text{H}_2\text{O}$ might be described as a framework made up of isolated $[\text{Mg}(\text{H}_2\text{O})_6 \cdot 2(\text{HPO}_3)]^{2-}$ and $[\text{NH}_4]^+$ units that are stabilized by an intricate network of hydrogen bonds (Table 2). Figs. 2 and 3 depict projections of the crystal structure. The three polyhedra $\text{Mg}(\text{H}_2\text{O})_6$, HPO_3 and NH_4 lie on a plane parallel to (010). The hydrogen-bond network ensures the interactions between two neighbouring planes.

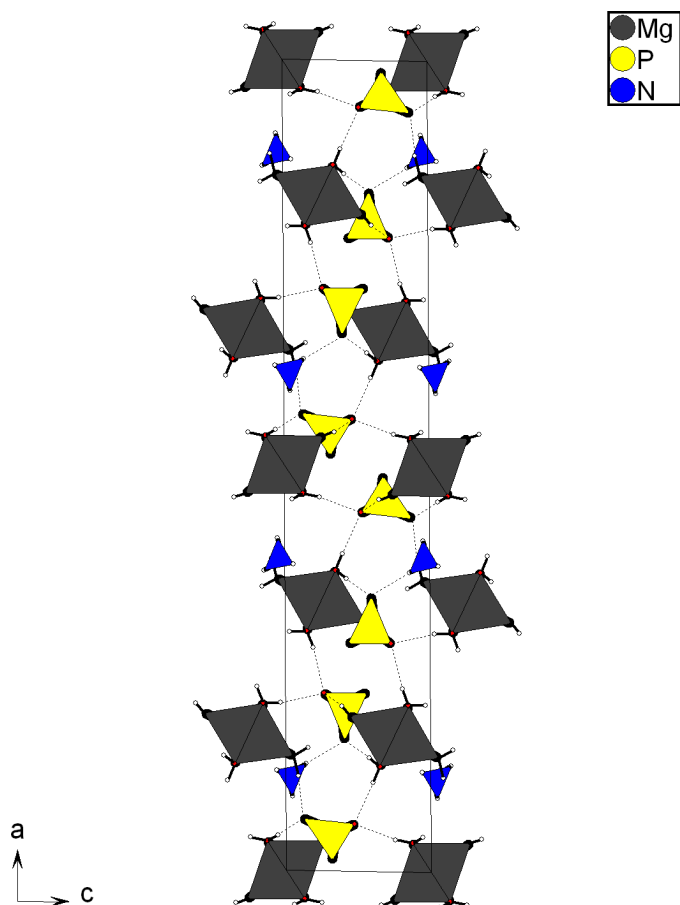


Figure 3
Projection of the crystal structure along *b*. Dashed lines indicate hydrogen bonds.

Experimental

MgO (10 mg) was dissolved in H_3PO_3 (10 ml) to which aqueous ammonia solution (around 5 ml, 0.4 M) was added. The solution was heated for 2 h at 300 K and was then left to stand at room temperature. After a week, colourless crystals of $(\text{NH}_4)_2\text{Mg}_3(\text{HPO}_3)_4 \cdot 18\text{H}_2\text{O}$ deposited. They were filtered off and washed with an ethanol–water (80:20) solution.

Crystal data

$(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6]_3(\text{HPO}_3)_4$
 $M_r = 753.21$
 Monoclinic, *C2/m*
 $a = 34.330$ (3) Å
 $b = 7.0380$ (3) Å
 $c = 6.1666$ (3) Å
 $\beta = 91.377$ (6)°
 $V = 1489.51$ (16) Å³
 $Z = 2$

$D_x = 1.679$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 72 reflections
 $\theta = 5.1$ –27.5°
 $\mu = 0.43$ mm⁻¹
 $T = 293$ (2) K
 Prism, colourless
 0.45 × 0.45 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Siemens, 1996)
 $T_{\min} = 0.831$, $T_{\max} = 0.848$
 4735 measured reflections
 1799 independent reflections

1687 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -44 \rightarrow 41$
 $k = -9 \rightarrow 9$
 $l = -7 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.064$
 $S = 1.11$
 1799 reflections
 158 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.6624P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

P1—O1	1.5235 (8)	Mg1—O6	2.0545 (9)
P1—O2	1.5261 (11)	Mg1—O7	2.0793 (13)
P1—H1	1.232 (18)	Mg1—O8	2.0929 (9)
P2—O4	1.5240 (8)	Mg1—O5	2.0973 (12)
P2—O3	1.5328 (11)	Mg2—O10	2.0504 (12)
P2—H2	1.267 (19)	Mg2—O9	2.0737 (9)
O1 ⁱ —P1—O1	112.41 (6)	O4 ⁱⁱ —P2—O4	112.92 (6)
O1—P1—O2	112.33 (4)	O4—P2—O3	111.67 (4)
O1 ⁱ —P1—H1	107.1 (4)	O4—P2—H2	106.6 (4)
O2—P1—H1	105.0 (9)	O3—P2—H2	106.8 (9)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O8—H81 \cdots O3	0.75 (2)	1.98 (2)	2.7227 (12)	168 (2)
O8—H82 \cdots O1	0.77 (2)	1.93 (2)	2.6883 (12)	173 (2)
O10—H100 \cdots O1	0.85 (2)	1.83 (2)	2.6707 (10)	169 (2)
N1—H110 \cdots O3	0.90 (3)	1.90 (3)	2.799 (2)	179 (2)
O5—H5 \cdots O4 ⁱ	0.87 (2)	1.81 (2)	2.6758 (10)	169 (2)
O6—H62 \cdots O4 ^v	0.80 (2)	1.94 (2)	2.7193 (12)	166 (2)
O6—H61 \cdots O4 ^{vi}	0.75 (2)	2.00 (2)	2.7436 (12)	170 (2)
O7—H71 \cdots O5 ^{vii}	0.71 (3)	2.23 (3)	2.9363 (19)	172 (3)
O7—H72 \cdots O2 ^{vii}	0.87 (3)	1.80 (3)	2.6657 (18)	172 (2)
O9—H91 \cdots O2 ^{iv}	0.85 (2)	1.87 (2)	2.7207 (12)	173 (2)
N1—H112 \cdots O8 ^{viii}	0.87 (2)	2.20 (2)	3.0242 (17)	157 (2)

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

H atoms were found in difference Fourier maps and refined isotropically without any restraints.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *EVALCCD* (Duisenberg, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97*.

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Brandenburg, K. (1999). *DIAMOND*. Version. 2.1c. Crystal Impact GbR, Bonn, Germany.
- Corbridge, D. E. C. (1956). *Acta Cryst.* **9**, 991–994.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- El Bali, B., Essehli, R., Capitelli, F. & Lachkar, M. (2005). *Acta Cryst.* **E61**, i52–i54.
- Essehli, R., Lachkar, M., Svoboda, I., Fuess, H. & El Bali, B. (2005). *Acta Cryst.* **E61**, i64–i66.
- Nonius. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Ortiz-Avila, C. Y., Squattrito, P. J., Shieh, M. & Clearfield, A. (1989). *Inorg. Chem.* **28**, 2608–2615.
- Ouarsal, R., Alaoui, T. A., Lachkar, M., Dusek, M., Fejfarova, K. & El Bali, B. (2003). *Acta Cryst.* **E59**, i33–i35.
- Ouarsal, R., Essehli, R., Lachkar, M., Zenkouar, M., Dusek, M., Fejfarova, K. & El Bali, B. (2004). *Acta Cryst.* **E60**, i66–i68.
- Powell, D. R., Smith, S. K. & Farrar, T. C. (1994). *Acta Cryst.* **C50**, 342–346.
- Rafiq, M., Durand, J. & le Cot, L. (1982). *Z. Anorg. Allg. Chem.* **484**, 187–194.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *SADABS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.