

## Bis(ammonium) tris(hexaaqua-magnesium) tetrakis(hydrogen phosphite)

Khaoulani Idrissi Abdallah,<sup>a</sup> Saadi Mohamed,<sup>b</sup> Rafiq Mohamed<sup>a</sup> and Guelzim Abdelhalim<sup>c\*</sup>

<sup>a</sup>Laboratoire des Matériaux et Protection de l'Environnement, Faculté des Sciences Dhar El Mehraz, Fés, Morocco, <sup>b</sup>Laboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V Agdal, Avenue Ibn Batouta, BP 1014, Rabat, Morocco, and <sup>c</sup>Laboratoire de Dynamique et Structure des Matériaux Moléculaires, UMR 8024, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France  
Correspondence e-mail: halim.guelzim@univ-lille1.fr

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The structure of the title compound,  $(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6]_3(\text{HPO}_3)_4$ , consists of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  and  $(\text{NH}_4)^+$  cations and  $(\text{HPO}_3)^{2-}$  anions held together by an intricate network of hydrogen bonds involving all H atoms except for one linked directly to a P atom. The  $\text{Mg}^{2+}$  cations are octahedrally coordinated by six water molecules. One of the Mg atoms is located on a site with  $2/m$  symmetry, whereas the other Mg atom and the P and N atoms occupy sites with  $m$  symmetry.

### Comment

Phosphites of inorganic cations have been described in several papers, notably those containing the hydrogenophosphite  $\text{HPO}_3^{2-}$  anion:  $\text{Mg}(\text{HPO}_3)\cdot 6\text{H}_2\text{O}$  (Corbridge, 1956),  $\text{Cu}(\text{HPO}_3)\cdot 2\text{H}_2\text{O}$  (Handlovič, 1969),  $\text{Na}_2(\text{HPO}_3)\cdot 5\text{H}_2\text{O}$  (Colton & Henn, 1971),  $\text{Sn}(\text{HPO}_3)$  (McDonald & Eriks, 1980),  $\text{Sb}_2(\text{HPO}_3)_3$  (Loub & Paulus, 1981),  $\text{Ga}_2(\text{HPO}_3)_3\cdot 4\text{H}_2\text{O}$  (Morris *et al.*, 1992),  $[\text{Mg}(\text{H}_2\text{O})_6](\text{HPO}_3)$  (Powell *et al.*, 1994),  $\text{Al}_2(\text{HPO}_3)_3$  and  $\text{Ga}_2(\text{HPO}_3)_3$  (Morris *et al.*, 1994), and  $\text{Fe}_{11}(\text{HPO}_3)_8(\text{OH})_6$  and  $\text{Mn}_{11}(\text{HPO}_3)_8(\text{OH})_6$  (Attfield *et al.*, 1994). However, mixed phosphites have received less attention and only a few compounds containing the dihydrogenophosphite anion  $\text{H}_2\text{PO}_3^-$  are known:  $\text{CoNa}(\text{H}_2\text{PO}_3)_3\cdot \text{H}_2\text{O}$  (Kratochvíl *et al.*, 1982),  $\text{MnNa}(\text{H}_2\text{PO}_3)_3\cdot \text{H}_2\text{O}$  (Chmelíková *et al.*, 1986),  $\text{NaZn}(\text{H}_2\text{PO}_3)_3\cdot \text{H}_2\text{O}$  (Ouarsal *et al.*, 2002) and  $\text{NaMg}(\text{H}_2\text{PO}_3)_3\cdot \text{H}_2\text{O}$  (Ouarsal *et al.*, 2003). To date, three mixed hydrogenophosphites have been reported, namely  $\text{LiTi}(\text{HPO}_3)$  (Rafiq *et al.*, 1981), and  $\text{Zn}_3\text{K}_2(\text{HPO}_3)_4$  and  $\text{Zn}_3\text{Ba}(\text{HPO}_3)_4\cdot 6\text{H}_2\text{O}$  (Ortiz-Avila *et al.*, 1989). In this paper, we report the crystal structure of a new mixed hydrogenophosphite,  $(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6]_3(\text{HPO}_3)_4$ . This compound was isolated during an investigation of the interactions between diammonium hydrogenophosphite monohydrate, magnesium chloride hexahydrate and phosphorous acid.

The asymmetric unit contains two crystallographically distinct Mg sites ( $m$  and  $2/m$ ), two P sites ( $m$ ), one N site ( $m$ ), ten O sites (1 and  $m$ ) and 15 H sites (1 and  $m$ ). Symmetry operations generate the complete  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations,  $(\text{HPO}_3)^{2-}$  anions and  $(\text{NH}_4)^+$  cation, as depicted in Fig. 1. The hydrogenophosphite anions show their usual pseudo-pyramidal geometry [mean P—O = 1.529 (2) Å and mean O—P—O = 112.3 (1)°] (Harrison, 2003). The P—O bond length of 1.529 (2) Å is in good agreement with the distance of 1.519 Å obtained from theoretical calculations (Farrar & Trudeau, 1990) for an isolated phosphite anion. The P—H distances (1.296 and 1.294 Å) compare favourably with the value calculated by statistical evaluation of the geometry of inorganic phosphites (1.30 Å; Loub, 1991). They are also comparable with the P—H distances in  $\text{Fe}_{11}(\text{HPO}_3)_8(\text{OH})_6$  (1.298 Å) and  $\text{Mn}_{11}(\text{HPO}_3)_8(\text{OH})_6$  (1.29 Å) (Attfield *et al.*, 1994), and in  $\text{NaMg}(\text{H}_2\text{PO}_3)_3\cdot \text{H}_2\text{O}$  (1.29 Å; Ouarsal *et al.*, 2003), but are shorter than those found in other phosphites, such as  $\text{LiTi}(\text{HPO}_3)$  (1.37 Å; Rafiq *et al.*, 1981) and  $[\text{Mg}(\text{H}_2\text{O})_6](\text{HPO}_3)$  (1.399 Å; Powell *et al.*, 1994).

The coordination around the two independent Mg1 and Mg2 atoms is quite similar. Each Mg atom is strongly coordinated by six water molecules, forming a slightly distorted octahedron. The Mg2 environment has an unusual octahedral geometry, with two apical Mg—O distances [2.053 (2) Å] shorter than the four equatorial Mg—O distances [2.076 (1) Å].

Both water H atoms bonded to atoms O5, O7, O8, O9 and O10, and one H atom bonded to atom O6, are involved in hydrogen bonding to the O atoms of the phosphites. The other H atom on atom O6 is directed toward atom O8 of an adjacent magnesium hydrate group, with an O...O distance of 2.939 (3) Å indicating a moderately strong interaction. The

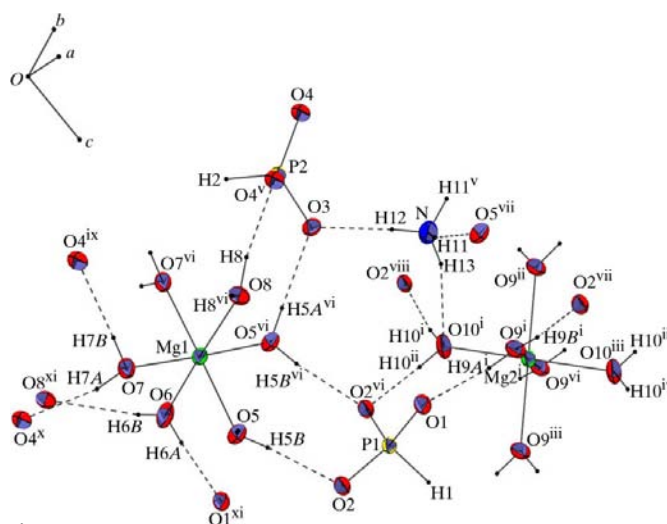


Figure 1

A view of the connectivity and hydrogen-bond network in the title compound. Displacement ellipsoids are drawn at the 35% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $x, -y + 1, 1 + z$ ; (ii)  $x, y, 1 + z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $1 - x, y, 1 - z$ ; (v)  $x, 1 - y, z$ ; (vi)  $x, -y, z$ ; (vii)  $x, -y, 1 + z$ ; (viii)  $x, 1 + y, z$ ; (ix)  $\frac{1}{2} - x, \frac{1}{2} - y, -z + 1$ ; (x)  $x, y - 1, z - 1$ ; (xi)  $x, y, z - 1$ .]

tetrahedral coordination of each phosphite O atom (except atom O3 linked to P2) is fulfilled through hydrogen bonds from three different  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations. Atom O3 is involved in two hydrogen bonds with two different water H atoms of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations and one hydrogen bond with the H atom of the  $\text{NH}_4^+$  cation. Atom H1 (H2) directly bonded to P1 (P2) is over 2.7 Å (2.8 Å) away from the closest O atom, indicating the absence of a hydrogen bond. The  $\text{NH}_4^+$  cation is an almost regular tetrahedron, with four comparable N—H distances ranging from 0.86 to 0.89 Å and comparable angles varying from 106 to 111°. The H atoms are involved in two hydrogen bonds of equal length [2.17 (3) Å] with water atoms O5 and O5<sup>i</sup>, and in two different hydrogen bonds with atoms O10(water) [2.36 (4) Å] and O3 [1.94 (3) Å].

The Mg—O bond lengths and O—Mg—O angles are generally as expected, with mean distances and angles of 2.080 Å and 89.78°, respectively, for Mg1, and 2.068 Å and 90°, respectively, for Mg2. These mean values agree well with those already found for  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ , notably in the phosphites  $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$  (2.086 Å and 90.90°; Ouarsal *et al.*, 2003) and  $[\text{Mg}(\text{H}_2\text{O})_6](\text{HPO}_3)$  (2.079 Å and 89.63°; Powell *et al.*, 1994), and in the phosphates  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  (2.083 Å and 89.82°; Sutor, 1967),  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (2.087 Å and 90.03°; Abbona *et al.*, 1984) and  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (2.071 Å and 90.85°; Whitaker & Jeffery, 1970).

**Experimental**

A sample of  $(\text{NH}_4)_2\text{HPO}_3 \cdot \text{H}_2\text{O}$  (2.5 g) was prepared by neutralization of phosphorous acid ( $\text{H}_3\text{PO}_3$ ) with ammonium hydroxide. The sample was dissolved in water (10 ml) and this solution was then added to a 150 ml stirred aqueous solution of  $\text{MgCl}_2$  (containing less than 0.1 g of Mg). The resulting solution was evaporated slowly at 313 K. After a few days, white crystals appeared as rectangular parallelepipeds.

*Crystal data*

$(\text{NH}_4)_2[\text{Mg}(\text{H}_2\text{O})_6]_3(\text{HPO}_3)_4$   
 $M_r = 753.21$   
 Monoclinic,  $C2/m$   
 $a = 34.364$  (9) Å  
 $b = 7.045$  (2) Å  
 $c = 6.1736$  (17) Å  
 $\beta = 91.349$  (4)°  
 $V = 1494.2$  (7) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.674$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1017 reflections  
 $\theta = 3.0\text{--}25.3^\circ$   
 $\mu = 0.43$  mm<sup>-1</sup>  
 $T = 289$  (2) K  
 Parallelepiped, white  
 $0.5 \times 0.35 \times 0.25$  mm

*Data collection*

Bruker SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.761$ ,  $T_{\text{max}} = 0.899$   
 6601 measured reflections

2083 independent reflections  
 1677 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\text{max}} = 29.3^\circ$   
 $h = -45 \rightarrow 47$   
 $k = -9 \rightarrow 9$   
 $l = -8 \rightarrow 8$

*Refinement*

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.092$   
 $S = 1.03$   
 2083 reflections  
 158 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.9053P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.29$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.39$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

P1—O2	1.5246 (12)	Mg1—O6	2.082 (2)
P1—O1	1.5281 (17)	Mg1—O5	2.0948 (14)
P2—O4	1.5258 (12)	Mg1—O8	2.0965 (19)
P2—O3	1.5371 (17)	Mg2—O10	2.0526 (19)
Mg1—O7	2.0585 (14)	Mg2—O9	2.0764 (13)
O2—P1—O2 <sup>i</sup>	112.30 (9)	O6—Mg1—O5	89.48 (6)
O2—P1—O1	112.33 (6)	O5—Mg1—O5 <sup>i</sup>	95.12 (8)
O4—P2—O4 <sup>ii</sup>	112.84 (10)	O7—Mg1—O8	90.15 (6)
O4—P2—O3	111.73 (6)	O6—Mg1—O8	178.16 (8)
O7—Mg1—O7 <sup>i</sup>	92.00 (8)	O5—Mg1—O8	89.27 (6)
O7—Mg1—O6	91.13 (6)	O10—Mg2—O9	86.84 (6)
O7—Mg1—O5	86.44 (6)	O9—Mg2—O9 <sup>ii</sup>	89.41 (8)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N—H11 <sup>..</sup> —O5 <sup>i</sup>	0.89 (3)	2.16 (3)	3.026 (3)	162 (2)
N—H12 <sup>..</sup> —O3	0.86 (3)	1.94 (3)	2.803 (3)	175 (3)
N—H13 <sup>..</sup> —O10	0.89 (4)	2.34 (4)	3.201 (4)	162 (3)
O5—H5A <sup>..</sup> —O3	0.830 (16)	1.898 (16)	2.7244 (18)	174 (2)
O5—H5B <sup>..</sup> —O2	0.821 (16)	1.873 (16)	2.6898 (18)	173 (2)
O6—H6A <sup>..</sup> —O1 <sup>ii</sup>	0.835 (18)	1.841 (18)	2.673 (3)	175 (3)
O6—H6B <sup>..</sup> —O8 <sup>iii</sup>	0.814 (18)	2.13 (2)	2.936 (3)	170 (4)
O7—H7A <sup>..</sup> —O4 <sup>ii</sup>	0.828 (16)	1.906 (17)	2.7212 (18)	168 (2)
O7—H7B <sup>..</sup> —O4 <sup>iii</sup>	0.820 (17)	1.928 (18)	2.7435 (18)	173 (3)
O8—H8 <sup>..</sup> —O4 <sup>iv</sup>	0.85 (2)	1.85 (2)	2.6807 (16)	169 (2)
O9—H9A <sup>..</sup> —O1	0.83 (3)	1.89 (3)	2.7242 (18)	175 (2)
O9—H9B <sup>..</sup> —O2 <sup>v</sup>	0.843 (17)	1.895 (17)	2.7325 (18)	172 (2)
O10—H10 <sup>..</sup> —O2 <sup>vi</sup>	0.81 (2)	1.87 (2)	2.6749 (16)	170 (2)

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

The H atoms were located in difference maps. Their positions were refined without any constraints, except for H5A/B, H6A/B, H7A/B and H9A/B, for which the O—H distances were restrained to 0.85 (2) Å. Individual isotropic displacement parameters were refined for the H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1091). Services for accessing these data are described at the back of the journal.

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