

Pentaguanidinium monohydrogen-diphosphopentamolybdate(VI) 2.5-hydrate, $(\text{CH}_6\text{N}_3)_5[\text{HP}_2\text{Mo}_5\text{O}_{23}]\cdot 2.5\text{H}_2\text{O}$: hydrogen bonding and π -stacking in guanidinium cations

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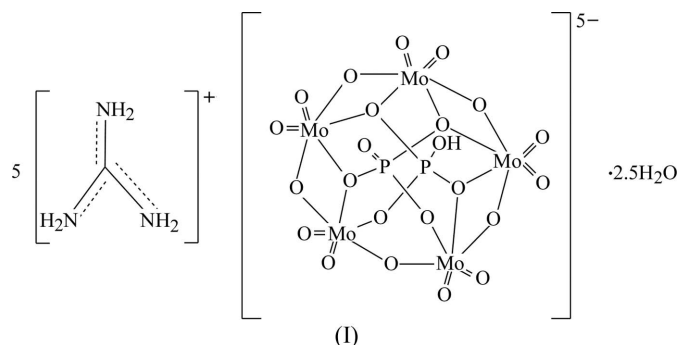
The asymmetric unit of the title compound consists of two crystallographically independent, but structurally identical, $[\text{HP}_2\text{Mo}_5\text{O}_{23}]^{5-}$ anions, ten guanidinium cations and five water molecules. Each singly protonated diphosphopentamolybdate(VI) anion retains the typical geometry of a ring of five edge-sharing MoO_6 octahedra [$\text{Mo}\cdots\text{Mo} = 3.3265(8)–3.4029(10) \text{ \AA}$], except for one corner-sharing link [$\text{Mo}\cdots\text{Mo} = 3.6642(7)$ and $3.6826(8) \text{ \AA}$]. Two capping PO_4 tetrahedra share corners with the five octahedra. Despite being surrounded by an extensive network of hydrogen bonds, predominantly from the guanidinium cations, short $\text{P}–\text{O}–\text{H}\cdots\text{O}=\text{P}$ contacts [$\text{O}\cdots\text{O} = 2.519(7)$ and $2.457(7) \text{ \AA}$] associate the anions into infinite columns generated by the c -glide. In addition to their heavy involvement in hydrogen bonding, with all $\text{N}–\text{H}$ donors being utilized, the guanidinium cations assemble into extensive π -stacked columns with an average interplanar spacing of 3.53 \AA .

Comment

The aim of our work is to study how the guanidinium cation, with its high hydrogen-bond donating potential, influences the packing of the highly oxygenated monohydrogenphosphomolybdate pentaanion.

Previous structural studies (Aranzabe *et al.*, 1997; Upreti & Ramanan, 2006; Fischer *et al.*, 1974) on the $[\text{HP}_2\text{Mo}_5\text{O}_{23}]^{5-}$ anion have shown that, while the $\text{P}–\text{OH}$ group does have a tendency to associate with the $\text{O}_3\text{P}=\text{O}$ region in an adjacent anion, this is not always the case. In the title compound, (I) (Fig. 1), short $\text{P}–\text{OH}\cdots\text{O}=\text{P}$ contacts link the anions into infinite chains (Fig. 2 and Table 1). This is also the case in the bisethylenetriammonium salt (Aranzabe *et al.*, 1997) and possibly more surprisingly the pentasodium salt (Hedman & Strandberg, 1979). However, the pentaammonium salt (Fischer *et al.*, 1974) shows a slight modification of this

arrangement, with the $\text{P}–\text{OH}$ group interacting with a $\text{P}–\text{O}–\text{Mo}$ bridging O atom to arrange the anions into chains, whilst direct contact between the phosphate groups is lost in the dianilinium salt as hydrogen-bonded water mediates between the phosphate regions. In all these cases, it is the cation–anion interaction that orchestrates the crystal packing and, taken by themselves, the anion–anion and cation–cation interactions would be energetically destabilizing, as established by D’Oria *et al.* (2012).



In (I), the space between the polyanions is occupied mainly by guanidinium cations, which are arranged in undulating

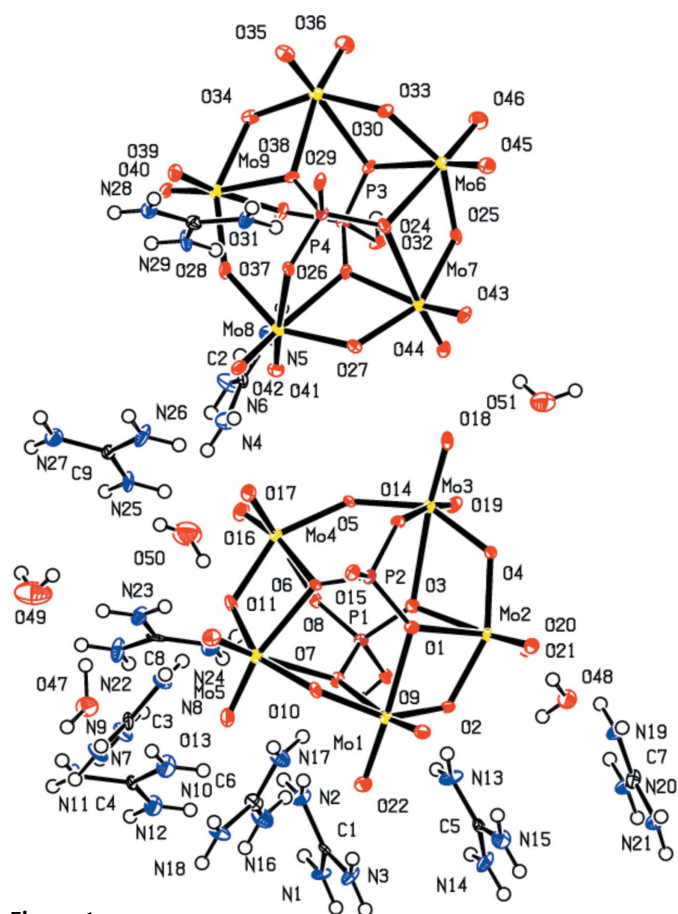


Figure 1

A view of the asymmetric unit of (I), containing two crystallographically independent, but structurally identical, $[\text{HP}_2\text{Mo}_5\text{O}_{23}]^{5-}$ anions, ten guanidinium cations and five water molecules, with displacement ellipsoids drawn at the 50% probability level.

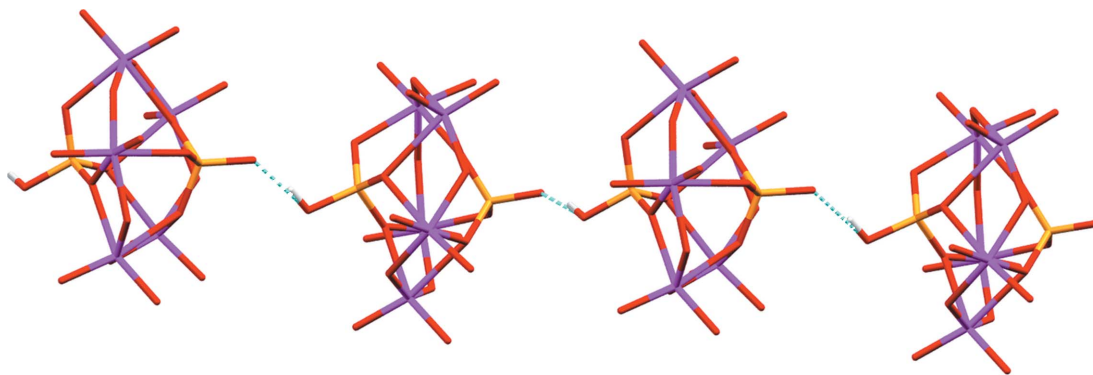


Figure 2

The P—H...O=P hydrogen bonds in (I) (dashed lines), linking the $[\text{HP}_2\text{Mo}_5\text{O}_{23}]^{5-}$ anions along c .

columns so that their π -systems overlap (Fig. 3). All guanidinium H atoms are involved in N—H...O hydrogen bonds except for one, which is directed edge-on towards the π -cloud of an adjacent guanidinium cation. The N—H...O hydrogen bonds can be classified into two types, *viz.* N—H...O_{water} [N...O = 2.912 (9)–3.162 (10) Å] and N—H...O, which can be further subdivided into singly [N...O = 2.758 (8)–3.162 (8) Å], bifurcated [N...O = 2.888 (8)–3.274 (7) Å], of which there are nine, and trifurcated [N...O = 2.915 (8)–3.229 (7) Å] hydrogen-bonded species, of which there are two. Also, the water molecules act as hydrogen-bond donors [water–oxide

O—H...O 2.776 (8)–3.087 (8) Å and water–water O—H...O = 2.956 (10)–3.162 (10) Å].

The Mo...P distances in (I) are in the range 3.277 (2)–3.643 (2) Å, and the P...P distances are 3.721 (2) and 3.738 (2) Å. Aranzabe *et al.* (1997) observed that the P...P distance shortens as the protonation state of the anion increases. However, the P...P distances in (I) are both significantly shorter than the equivalent distance in a doubly protonated anion (Aranzabe *et al.*, 1997), suggesting that this distance is susceptible to influences other than protonation. The attachment of an H atom to one of the terminal O atoms elongates the P—O distance and shortens the remaining P—O bonds compared with the unprotonated phosphate group (Table 2).

The Mo—O bond lengths of (I) vary according to whether they are terminal [1.686 (5)–1.736 (5) Å], Mo—O—Mo bridging [1.906 (4)–1.966 (5) Å] or Mo—O—P bridging [2.181 (4)–2.438 (5) Å], with each Mo atom having two of the three types of bond. The Mo atoms of the pentagonal ring are nearly in the same plane and no significant deviations are observed as a consequence of the protonation.

Experimental

Colourless needles of (I) were obtained by adding an aqueous 0.1 M solution of guanidinium carbonate (4 ml) to a 0.1 M solution of $\text{H}_3[\text{P}(\text{Mo}_3\text{O}_{10})_4]$ (1 ml) in water and allowing the solution to evaporate over a period of 5 d.

Crystal data

$(\text{CH}_6\text{N}_3)_5[\text{HP}_2\text{Mo}_5\text{O}_{23}] \cdot 2.5\text{H}_2\text{O}$
 $M_r = 1256.13$
 Monoclinic, $P2_1/c$
 $a = 23.0859$ (10) Å
 $b = 19.2656$ (9) Å
 $c = 15.7659$ (8) Å
 $\beta = 92.873$ (4)°

$V = 7003.3$ (6) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 1.95$ mm⁻¹
 $T = 100$ K
 $0.25 \times 0.02 \times 0.02$ mm

Data collection

Agilent Xcalibur Sapphire2
 diffractometer (large Be window)
 Absorption correction: multi-scan
 (*CrysAlis PRO*; Agilent, 2011)
 $T_{\text{min}} = 0.642$, $T_{\text{max}} = 0.962$

27434 measured reflections
 13733 independent reflections
 9661 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$

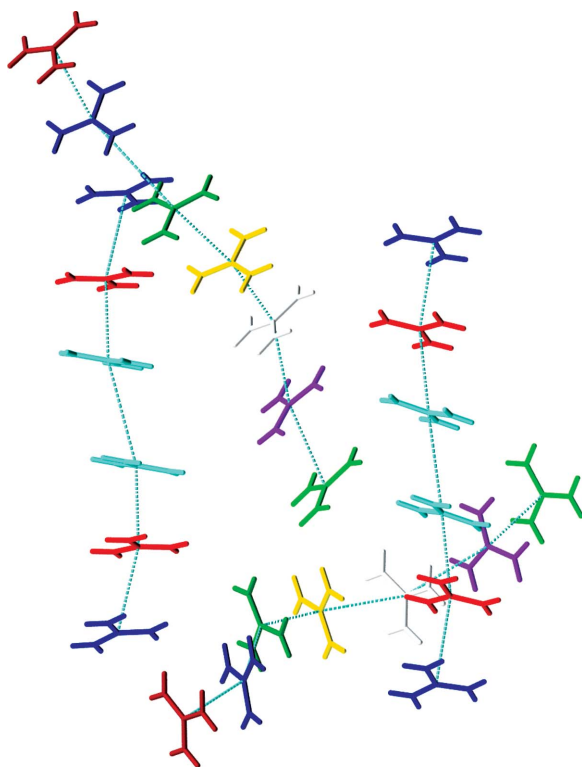


Figure 3

A view down c of the guanidinium π -stacks in (I), with dashed lines showing the interactions. The different colours indicate different unique cations.

Table 1

P—OH...O=P hydrogen-bond geometry (Å, °).

<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>
O9—H9...O15 ⁱ	0.84	1.71	2.519 (7)	160
O32—H32...O38 ⁱⁱ	0.84	1.63	2.457 (7)	169

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

Table 2

Selected geometric parameters (Å, °).

O1—P2	1.568 (5)	O24—P4	1.550 (5)
O3—P1	1.537 (5)	O26—P3	1.547 (5)
O6—P2	1.561 (5)	O29—P4	1.563 (5)
O7—P1	1.548 (5)	O30—P3	1.544 (5)
O8—P1	1.518 (5)	O31—P3	1.514 (5)
O9—P1	1.560 (5)	O32—P3	1.548 (5)
O14—P2	1.523 (5)	O37—P4	1.530 (5)
O15—P2	1.511 (5)	O38—P4	1.514 (5)
O8—P1—O3	109.9 (3)	O31—P3—O32	111.7 (3)
O8—P1—O9	110.5 (3)	O30—P3—O32	110.8 (3)
O7—P1—O9	110.5 (3)	O26—P3—O32	104.3 (3)
O15—P2—O14	110.3 (3)	O38—P4—O37	110.3 (3)
O14—P2—O6	106.7 (3)	O38—P4—O24	111.3 (3)
O15—P2—O1	112.0 (3)	O38—P4—O29	109.8 (3)

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.049$$

$$wR(F^2) = 0.106$$

$$S = 1.04$$

13733 reflections

993 parameters

24 restraints

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 1.32 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -1.16 \text{ e } \text{Å}^{-3}$$

All of the guanidinium H atoms were initially placed in geometrically calculated positions assuming a planar geometry about the N atoms (AFIX 93 instruction of *SHELXL97*; Sheldrick, 2008) and refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$. An edge-to-face approach of the guanidiniums at N2 and N10 led to a clash of the H atoms and made it necessary to refine the H atoms of these two groups with N—H and H...H bond-length restraints of 0.88 (2) and 1.52 (1) Å, respectively, which allowed sp^3 distortion. Additionally, the interaction distances between C1 and the H atoms on N2 and between C4 and the H atoms on N10 were restrained to be equal within a tolerance of 0.01 Å. Both phosphate H atoms were placed in geometrically optimized positions and also refined using a riding model with rotational freedom about the parent P—O bond and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The water H atoms were located in difference

Fourier maps and, because of their large positional uncertainty, were refined with O—H and H...H distance restraints of 0.82 (1) and 1.34 (1) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O51})$, except for H51W/X, for which the $U_{\text{iso}}(\text{H})$ values were fixed at 0.034 Å². Additionally, the intermolecular distances between N4 and water H atoms H50X/W were restrained to be equal within a tolerance of 0.02 Å to prevent a clash with the H atom attached to N4. The crystal was an extremely thin needle and empirical absorption corrections were only partially successful, leaving significant electron density around the Mo atoms. It is thought that this is the reason why 12 reflections showed particularly bad F_o/F_c agreement and had to be omitted.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3013). Services for accessing these data are described at the back of the journal.

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