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Bis(3,5-dimethylpiperazinium) di-μ_5-hydrogenphosphato-penta-μ_2-oxo-pentakis[dioxomolybdenum(V)] dihydrate

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Key indicators

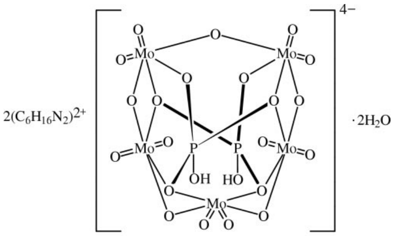
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.008 Å
Disorder in solvent or counterion
R factor = 0.034
wR factor = 0.095
Data-to-parameter ratio = 15.5

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

The dications and tetraanion in the title compound, $(C_6H_{16}N_2)_2[Mo_5O_{15}(HPO_4)_2]\cdot 2H_2O$, occupy special positions in the crystal structure. One of the independent cations lies on a site of $\overline{1}$ symmetry and the other lies on a site of 2 symmetry. The tetraanion, which has 2 site symmetry, consists of a five-unit ring of vertex/edge-sharing MoO_6 octahedra; the ring is capped by two P(OH) units on opposite sides. The anions are linked *via* hydrogen bonds involving the H atom of the hydrogenphosphate group into a zigzag chain running along the *c* axis. The chains are incorporated into the network structure through hydrogen bonds involving the cations and lattice water molecules.

Comment

Pentakis(trioxomolybdophosphate) polyanions feature a five-unit ring of MoO_6 octahedra, such that octahedra 1 and 2, 2 and 3, 3 and 4, and 4 and 5 share an edge, whereas octahedra 1 and 5 have only one common vertex (Harrison *et al.*, 1997*a*,*b*). The five-unit ring is capped on either side by the phosphate tetrahedron. This feature is also found in the closely related bis(piperazinium) pentakis(trioxomolybdo)bis(ethylphosphonate) dihydrate (Harrison *et al.*, 1997*a*) and bis(piperazinium) pentakis(trioxomolybdo)bis(phenylphosphonate) dihydrate (Harrison *et al.*, 1997*b*), whose structures are described as layered arrangements of the anionic clusters. The use of the 2,5-dimethylpiperazine cation with phosphoric acid in place of unsubstituted piperazine and ethyl- or phenylphosphonic acid yields a 2,5-dimethylpiperazinium salt of the anionic cluster, having a hydroxy group on the P atom. One of the independent cations lies on a site of $\overline{1}$ symmetry and the other lies on a site of 2 symmetry. The tetraanion has 2 site symmetry.



(I)

In the title compound, (I) (Fig. 1), the anions are linked *via* hydrogen bonds involving this hydroxy group into zigzag chains running along the *c* axis of the monoclinic cell (Fig. 2). These hydrogen bonds are significantly stronger than most of the other hydrogen bonds in the structure (Table 2); the latter consolidate the cations, anions and lattice water molecules into a three-dimensional network. The MoO_6 octahedra

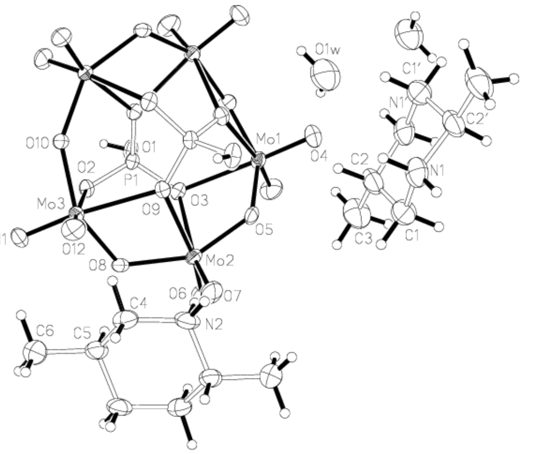


Figure 1
*ORTEP*II (Johnson, 1976) plot of (I), with displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The alternative component of the disordered cation has been omitted.

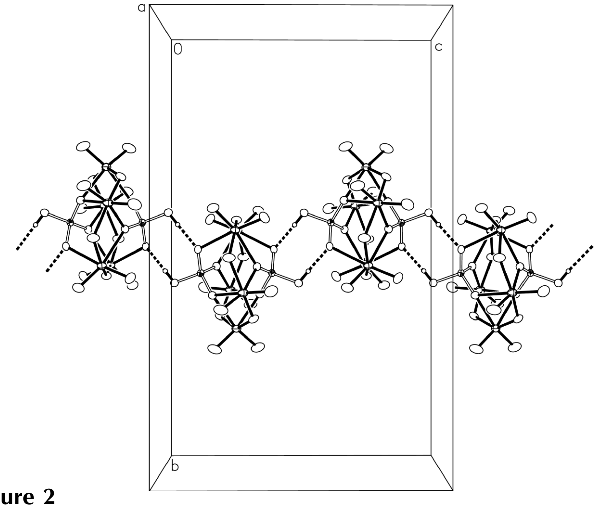


Figure 2
*ORTEP*II (Johnson, 1976) plot illustrating the linear chain structure arising from the inter-anion hydrogen bonds. H atoms are drawn as spheres of arbitrary radii.

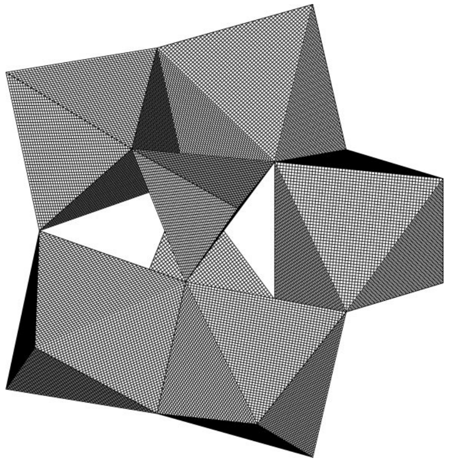


Figure 3
Polyhedral representation of the $[Mo_5O_{15}(HPO_4)_2]^{4-}$ anion.

making up the ring (Fig. 3) show bond dimensions similar to those reported previously (Harrison *et al.*, 1997*a*,*b*).

Experimental

The title compound was synthesized hydrothermally from molybdenum trioxide (0.14 g), 2,5-dimethylpiperazine (0.06 g), 85% phosphoric acid (0.17 g) and water (6 ml) in a 2:1:3:666 molar stoichiometry. The solution was heated for 4 d at 413 K in a 15 ml Teflon-lined bomb. The bomb was cooled to room temperature, affording well formed prismatic crystals in about 70% yield. Analysis found: C 12.84, H 3.46, N 4.97%; calculated for $C_{12}H_{38}Mo_5N_4O_{25}$: C 12.89, H 3.43, N 5.01%.

Crystal data

$(C_6H_{16}N_2)_2[Mo_5O_{15}(HPO_4)_2]\cdot 2H_2O$
$M_r = 1180.10$
Monoclinic, $C2/c$
$a = 10.8677$ (5) Å
$b = 21.960$ (1) Å
$c = 13.7160$ (6) Å
$\beta = 90.715$ (1)°
$V = 3273.1$ (3) Å^3
$Z = 4$
$D_x = 2.395$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6915 reflections
$\theta = 2.4$–27.0°
$\mu = 2.06$ mm^{-1}
$T = 298$ (2) K
Prism, colorless
0.32 × 0.26 × 0.20 mm

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.438$, $T_{\rm max} = 0.662$
9212 measured reflections
3538 independent reflections
3017 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.049$
$\theta_{\rm max} = 27.0°$
$h = -10 \rightarrow 13$
$k = -25 \rightarrow 27$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.095$
$S = 1.04$
3538 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.88$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.01$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O3	2.369 (3)	Mo2—O9	2.228 (3)
Mo1—O4	1.683 (4)	Mo3—O2	2.331 (3)
Mo1—O5	1.914 (3)	Mo3—O8	1.914 (3)
Mo2—O3	2.433 (3)	Mo3—O9	2.328 (3)
Mo2—O5	1.897 (3)	Mo3—O10	1.913 (1)
Mo2—O6	1.704 (4)	Mo3—O11	1.713 (3)
Mo2—O7	1.703 (4)	Mo3—O12	1.697 (3)
Mo2—O8	1.953 (3)		
O3—Mo1—O3$^{\rm i}$	81.9 (2)	O6—Mo2—O9	157.9 (2)
O3—Mo1—O4	168.2 (2)	O7—Mo2—O8	98.8 (2)
O3—Mo1—O4$^{\rm i}$	87.5 (2)	O7—Mo2—O9	96.0 (2)
O3—Mo1—O5	71.9 (1)	O8—Mo2—O9	72.5 (1)
O3—Mo1—O5$^{\rm i}$	81.2 (1)	O2—Mo3—O8	77.5 (1)
O4—Mo1—O4$^{\rm i}$	103.4 (3)	O2—Mo3—O9	86.6 (1)
O4—Mo1—O5	101.4 (2)	O2—Mo3—O10	78.9 (1)
O4—Mo1—O5$^{\rm i}$	100.6 (2)	O2—Mo3—O11	82.7 (1)
O5—Mo1—O5$^{\rm i}$	144.2 (2)	O2—Mo3—O12	173.8 (2)
O3—Mo2—O8	87.4 (1)	O8—Mo3—O9	70.9 (1)
O3—Mo2—O9	72.5 (1)	O8—Mo3—O10	147.4 (2)
O3—Mo2—O5	70.7 (1)	O8—Mo3—O11	97.6 (2)
O3—Mo2—O6	88.2 (2)	O8—Mo3—O12	103.4 (2)
O3—Mo2—O7	164.8 (2)	O9—Mo3—O10	85.6 (1)
O5—Mo2—O6	101.1 (2)	O9—Mo3—O11	165.8 (1)
O5—Mo2—O7	98.6 (2)	O9—Mo3—O12	87.9 (1)
O5—Mo2—O8	151.3 (1)	O10—Mo3—O11	101.4 (2)
O5—Mo2—O9	83.1 (1)	O10—Mo3—O12	97.8 (1)
O6—Mo2—O7	104.7 (2)	O11—Mo3—O12	103.1 (2)
O6—Mo2—O8	96.4 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O1-H1\cdots O2^{ii}}$	0.82	1.85	2.656 (4)	168
$\mathrm{O1W-H1W1\cdots O4}$	0.86	2.11	2.970 (7)	177
$\mathrm{N1-H1N1\cdots O10^{iii}}$	0.90	2.22	3.067 (9)	158
$\mathrm{N1-H1N2\cdots O1W^{iv}}$	0.90	1.69	2.59 (1)	172
$\mathrm{N1'-H1N3\cdots O6^{v}}$	0.90	2.16	2.825 (9)	130
$\mathrm{N1'-H1N4\cdots O1W}$	0.90	1.97	2.84 (1)	160
$\mathrm{N2-H2N1\cdots O8^{vi}}$	0.90	2.17	2.950 (6)	145
$\mathrm{N2-H2N1\cdots O11^{vi}}$	0.90	2.16	2.886 (6)	137
$\mathrm{N2-H2N2\cdots O7}$	0.90	2.01	2.872 (6)	160

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

The cation (N1/C1/C2/C3) that lies on the twofold axis is disordered, and the atoms constituting the ring were refined as six independent atoms (N1, N1′, C1, C1′, C2 and C2′) so as to restrain the ring in a chair-shaped conformation. The N—C═C—C bond distances were restrained to 1.50 (1) Å and the N···C═C···C 1,3-separations in the ring were kept at 2.45 (1) Å. The C2—C3 distance was similarly restrained. The temperature factors of the unprimed and primed atoms were constrained to be equal to each other. The ammonium and methylene H atoms were positioned geometrically and were treated using a riding-model approximation. The water H atoms were located using the HYDROGEN option (Nardelli, 1999) in the *WinGX* suite (Farrugia, 1999), but their positions were not refined. The displacement parameters of all H atoms were taken to be 1.2 times (1.5 for methyl H atoms) the equivalent isotropic displacement parameters of the atoms on which they were riding. The deepest hole in the electron-density difference map is 0.9 Å from atom Mo2.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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