Tetrakis(1,4-dimethylpyridinium) dodecamolybdophosphate nitrate

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In the title compound, $(C_7H_{10}N)_4[PMo_{12}O_{40}]NO_3$, the asymmetric unit contains two 1,4-dimethylpyridinium (DMP) cations, one half of a nitrate anion perpendicular to the mirror plane and one half of a dodecamolybdophosphate (PMo_{12}) anion. Because of orientational disorder, a crystallographic centre of symmetry appears at the central P atom of the PMo_{12} anion, although the PO_4 moiety has a tetrahedral structure and does not have a centre of symmetry. The PMo_{12} anions show a disordered 'pseudo-Keggin' structure and they are linked into an infinite three-dimensional assembly by DMP cations, *via* electrostatic forces and C—H···O interactions.

Comment

In crystal engineering and polyoxometallate (POM) chemistry, one of the major challenges is to establish reliable connections between new molecular and supramolecular structures on the basis of intermolecular interactions, because these materials may exhibit cooperative properties typically associated with POM network solids (Desiraju 1995; Coronado & Gómez-García, 1998). Ideally, one would like to identify substructural units in a target supermolecule that can be assembled from logically chosen precursor molecules. Here, we have attempted to use the normal method to realise such molecular assemblies. This paper deals with the preparation and crystal structure of the title supramolecular compound, (I), which was obtained from the reaction of 1,4-dimethylpyridinium iodide (DMPI) and Keggin type $H_3PMo_{12}O_{40}$.

(I)
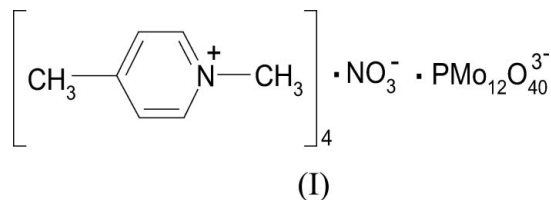
The asymmetric unit of (I) contains one half of a dodecamolybdophosphate anion (denoted PMo12; Fig. 1), one half of a nitrate anion perpendicular to the mirror plane, and two 1,4-dimethylpyridinium (DMP) cations (denoted DMP-*A* and DMP-*B*; Fig. 2). The PMo12 anion shows a disordered 'pseudo-Keggin' structure, but with local site symmetry $m\overline{3}m(O_h)$, instead of the tetrahedral symmetry of the α-Keggin molecule (Evans & Pope, 1984). This can be interpreted as orientational disorder of normal α-Keggin molecules over two positions related by an inversion centre (Attanasio *et*
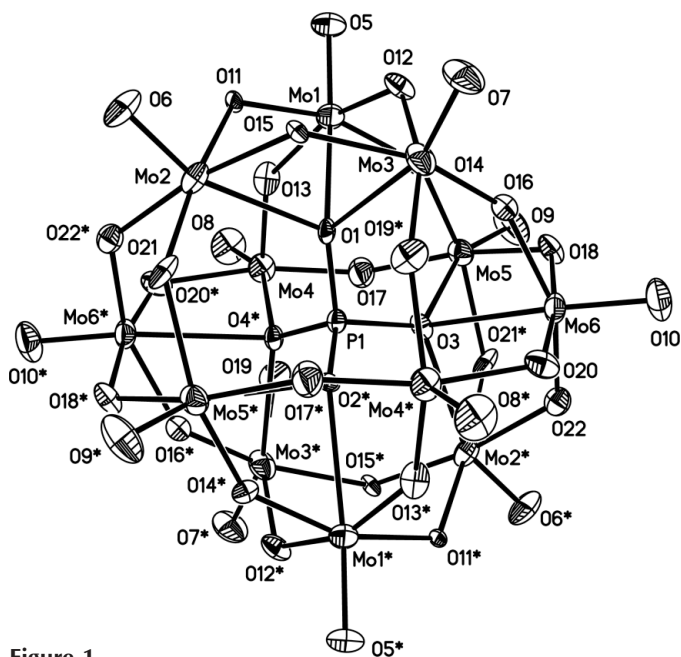
Figure 1
A view of the PMo_{12} anion of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The occupancy factors of atoms O1–O4 and O11–O22 are 50% and 46.6 (8)%, respectively. The other possible orientation of the central PO_4 moiety (O1*/O2/O3*/O4) and the other form of each of the disordered bridging O atoms (O11A–O22A) have been omitted for clarity. Atoms labelled with an asterisk (*) are at the symmetry position ($\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$).
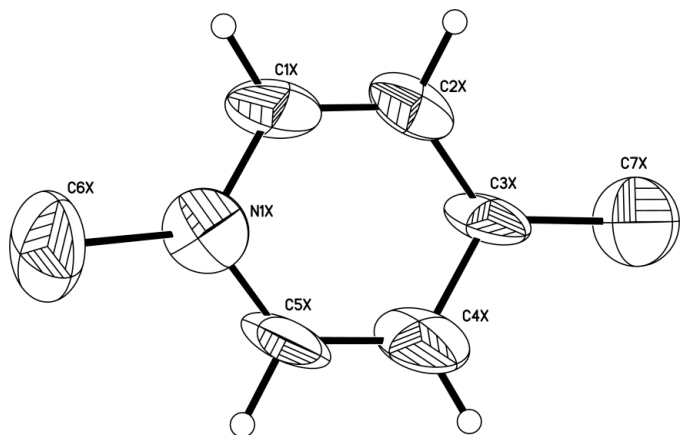

Figure 3
A partial packing diagram for (I), viewed along the c axis, showing DMP-A cations linking the PMo_{12} anions into layers parallel to the (001) plane. Weak hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 10% probability level.

Figure 2
The structure of one of the DMP cations of (I), with the atom-numbering scheme; X can be replaced with A or B. Displacement ellipsoids are drawn at the 30% probability level.

Figure 4
A partial packing diagram for (I), viewed down the a axis, showing DMP-B cations linking the PMo_{12} anions into layers parallel to the (100) plane. Weak hydrogen bonds are shown as dashed lines and displacement ellipsoids are drawn at the 10% probability level.

al., 1990). The PO_4 group is disordered, with the P atom at ($\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$) surrounded by a cube of O atoms at 1.501 (13)–1.547 (13) Å (Table 1), with each O site half-occupied. There are two possible combinations, O1/O2^i/O3/O4^i or O1^i/O2/O3^i/O4 [symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$]. A further investigation of the O atoms of the $PMo1_{12}$ anion revealed that all of the bridging O atoms are disordered over two sets of positions, O11–O22 and O11A–O22A, with site-occupancy factors of 46.64 (9)% and 53.36 (9)%, respectively. The large atomic displacement parameters of the nitrate ion suggest positional disorder. In the DMP cations, no disorder was found.
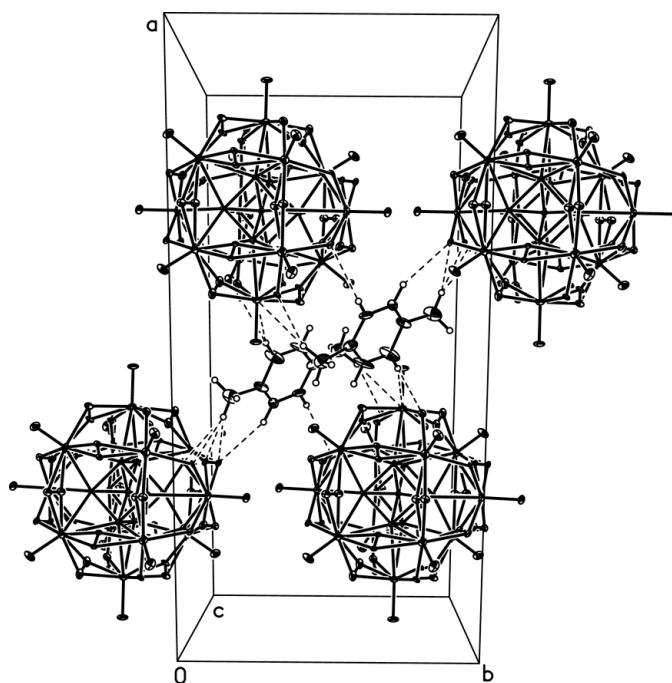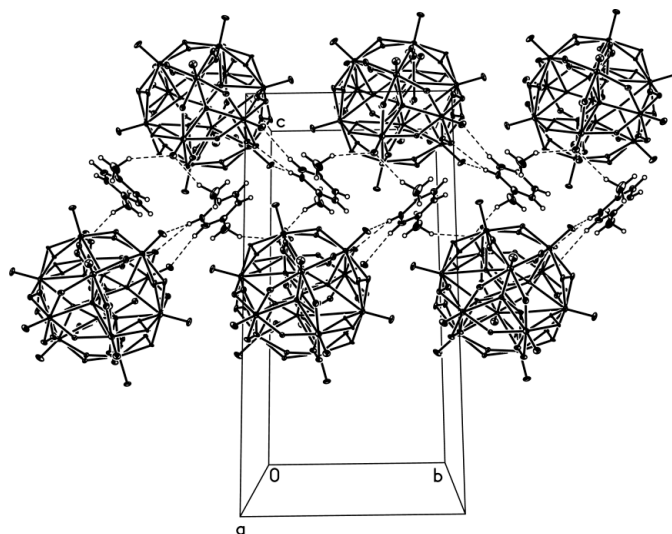
In the crystal structure of (I), the cations and anions are connected mainly by electrostatic forces. The *PLATON* program (Spek, 2003) suggests that there are no classical hydrogen bonds, but there are weak C—H$\cdots$O hydrogen bonds (Table 2; Krishnamohan Sharma & Desiraju, 1994). DMP-A cations and PMo_{12} anions form a layer structure parallel to the (001) plane (Fig. 3). Weak hydrogen bonds occur within the layers but do not exist between layers.

Similarly, DMP-*B* cations and PMo$_{12}$ anions form a layer structure parallel to the (100) plane (Fig. 4), and weak hydrogen bonds occur only within the layers. Thus, besides the electrostatic forces, weak hydrogen bonds help to link the anions and cations of (I) into an infinite three-dimensional network.

Experimental

All organic solvents and common materials used for the synthesis were of reagent grade and were used without further purification. H$_3$PMo$_{12}$O$_{40}$ was prepared according to the literature method of Rocchiccioli-Deltcheff *et al.* (1983). 1,4-Dimethylpyridinium iodide (DMPI) was prepared following the method of Ren *et al.* (2000). Compound (I) was prepared by mixing a 0.01 *M* aqueous solution of DMPI and a 0.01 *M* aqueous solution of H$_3$PMo$_{12}$O$_{40}$ (acidified by nitric acid to pH = 6) in the molar ratio of 3:1. The precipitate which formed was filtered off, dried and recrystallized from dimethylformamide (yield 82%). After 40 d of slow evaporation of dimethylformamide at room temperature, shiny black crystals of (I) were obtained. Elemental analysis, calculated: C 14.51, H 1.74, N 3.02%; found: C 15.42, H 1.99, N 3.16%.

Crystal data

(C$_7$H$_{10}$N)$_4$[Mo$_{12}$O$_{40}$P]NO$_3$	$D_x = 2.579$ Mg m^{-3}
$M_r = 2316.90$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 380
$a = 24.271$ (6) Å	reflections
$b = 11.200$ (3) Å	$\theta = 7.5-27.1°$
$c = 23.316$ (6) Å	$\mu = 2.56$ mm^{-1}
$\beta = 109.679$ (3)°	$T = 291$ (2) K
$V = 5968$ (3) Å^3	Needle, black
$Z = 4$	$0.27 \times 0.12 \times 0.11$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	6338 independent reflections
φ and ω scans	4283 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$R_{int} = 0.055$
	$\theta_{max} = 27.1°$
$T_{min} = 0.693$, $T_{max} = 0.757$	$h = -24 \rightarrow 30$
16 331 measured reflections	$k = -14 \rightarrow 13$
	$l = -23 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0788P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.081$	$+ 19.95P]$
$wR(F^2) = 0.183$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
6338 reflections	$\Delta\rho_{max} = 1.47$ e Å^{-3}
471 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
H-atom parameters constrained	Extinction correction: none

Table 1
Selected bond lengths (Å).

O1—P1	1.538 (13)	O3—P1	1.547 (13)
O1—Mo1	2.425 (13)	O3—Mo5	2.420 (12)
O1—Mo3	2.471 (13)	O3—Mo6	2.447 (13)
O1—Mo2	2.489 (12)	O3—Mo2^i	2.512 (13)
O2—P1	1.501 (13)	O4—P1	1.518 (13)
O2—Mo1	2.479 (12)	O4—Mo4^i	2.444 (14)
O2—Mo4	2.482 (14)	O4—Mo6	2.490 (12)
O2—Mo5	2.484 (12)	O4—Mo3	2.496 (13)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1*A*—H1*A*$\cdots$O11^{ii}	0.93	2.48	3.26 (3)	142
C2*A*—H2*A*$\cdots$O21^i	0.93	2.54	3.38 (3)	151
C4*A*—H4*A*$\cdots$O19*A*^{iii}	0.93	2.28	3.17 (4)	159
C6*A*—H6*B*$\cdots$O13*A*^{ii}	0.96	2.22	3.12 (4)	155
C7*A*—H7*A*$\cdots$O15^i	0.96	2.56	3.27 (3)	131
C7*A*—H7*A*$\cdots$O21^i	0.96	2.50	3.40 (4)	157
C7*A*—H7*A*$\cdots$O15*A*^{i}	0.96	2.52	3.31 (3)	140
C7*A*—H7*A*$\cdots$O21*A*^{i}	0.96	2.52	3.45 (4)	164
C1*B*—H1*B*$\cdots$O9^{iv}	0.93	2.44	3.34 (2)	162
C1*B*—H1*B*$\cdots$O18^{iv}	0.93	2.53	3.24 (2)	133
C2*B*—H2*B*$\cdots$O10^{iv}	0.93	2.45	3.37 (2)	172
C6*B*—H6*E*$\cdots$O7^v	0.96	2.49	3.30 (2)	142
C7*B*—H7*F*$\cdots$O7^{vi}	0.96	2.55	3.32 (2)	138

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

The assignment of Me—C (C3*X*) and Me—N (N1*X*) in the pyridine rings of the DMP cations could be made rationally from the displacement parameters. The disorder of the O atoms in the PMo$_{12}$ anions and the large atomic displacement parameters of the nitrate anions contributed to the high U_{eq}(max)/U_{eq}(min) values of some of the O atoms, so nine restraints of approximate isotropy (O1/O3/O14/O15/O16/O19*A*/O21/O22/O32) were used in the refinement to lower these values, and other geometric restraints (DFIX and DANG) were also used to make the geometry reasonable, contributing to the high R value (0.081). All H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å, and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for the other H atoms.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

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