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Key indicators

Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.073 \text{ \AA}$
 R factor = 0.106
 wR factor = 0.262
 Data-to-parameter ratio = 16.4

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

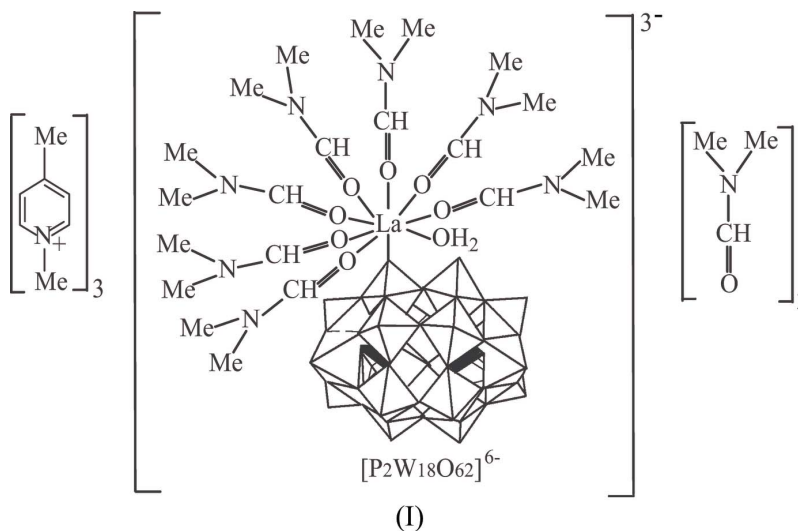
Tris(1,4-dimethylpyridinium) aquaheptakis-(dimethylformamide- κO)lanthanum(III) diphosphatooctadecatungsten dimethylformamide disolvate

In the title compound, $(\text{C}_7\text{H}_{10}\text{N})_3[\text{La}(\text{P}_2\text{W}_{18}\text{O}_{62})(\text{C}_3\text{H}_7\text{NO})_7(\text{H}_2\text{O})] \cdot 2\text{C}_3\text{H}_7\text{NO}$, 1,4-dimethylpyridinium cations, $[\text{La}(\text{DMF})_7(\text{H}_2\text{O})]^{3+}$ (DMF = dimethylformamide) complex cations and octadecatungstodiphosphate ($\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$) anions form an infinite three-dimensional assembly *via* La–O–W coordination bonds, electrostatic forces, and C–H···O and O–H···O hydrogen bonds.

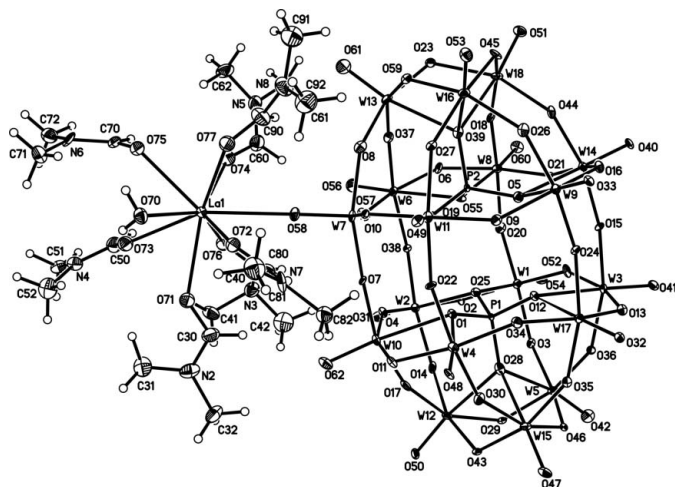
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Comment

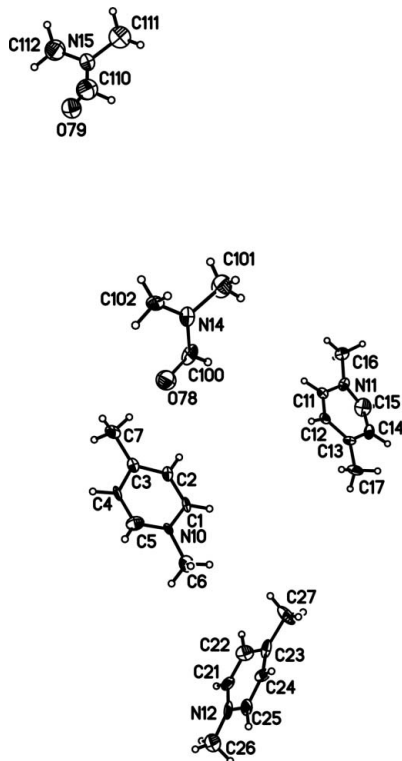
In crystal engineering and polyoxometalate chemistry, one of the major challenges is to establish reliable connections between new molecular and supramolecular structures on the basis of intermolecular interactions (Desiraju 1995; Niu *et al.*, 2003). In this paper we report the preparation and crystal structure of the title compound, (I).



The asymmetric unit of (I) consists of three 1,4-dimethylpyridinium (DMAP) cations, one $[\text{La}(\text{DMF})_7(\text{H}_2\text{O})]^{3+}$ complex cation (DMF = dimethylformamide), one octadecatungstodiphosphate anion ($\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$; abbreviated as POM) and two DMF solvent molecules. The La atom is nine-coordinated by seven O atoms from DMF, one O atom from water and one O atom from POM (Figs. 1 and 2), exhibiting a distorted tricapped trigonal-prismatic coordination geometry. The La1–O58 (from POM) bond distance is 2.70 (3) Å, which is longer than the other La–O coordinate bonds, 2.46 (4)–2.65 (4) Å. In the Dawson structure $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$, there are 18 terminal O atoms, which are only bonded to one W atom, and the W–O distances range from 1.62 (3) to 1.74 (3) Å. The bond distance of W7–O58 is 1.67 (3) Å, a median, indicating


Figure 1

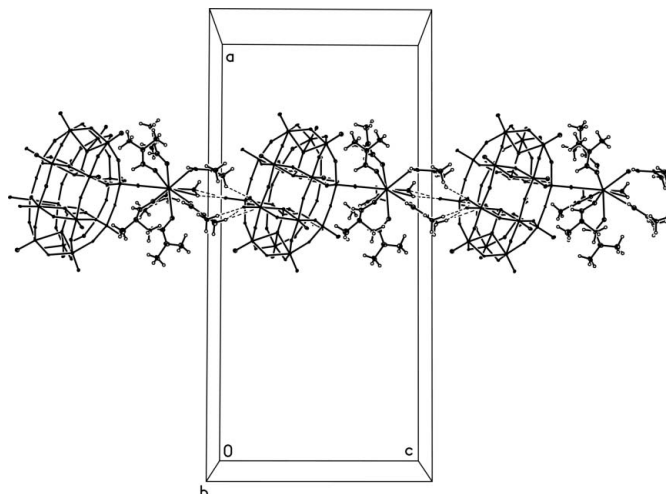
The $\text{La}(\text{DMF})_7(\text{H}_2\text{O})^{3+}$ cation and octadecatungstodiphosphate anion in the asymmetric unit of (I), showing 20% probability displacement ellipsoids.


Figure 2

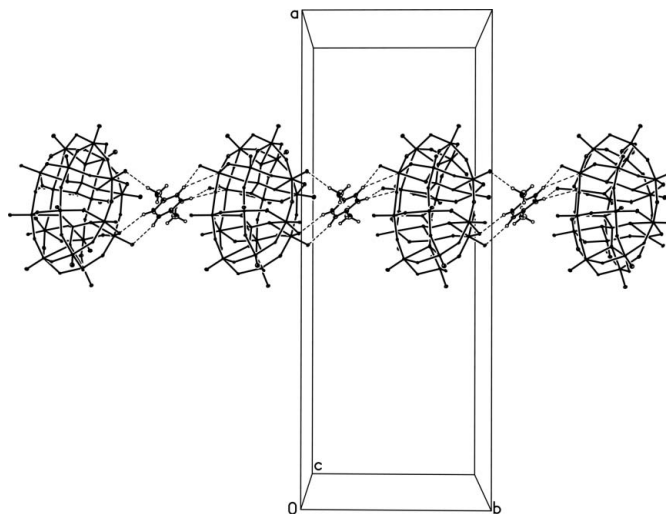
1,4-Dimethylpyridinium cations and DMF solvent molecules in the asymmetric unit of (I), showing 20% probability displacement ellipsoids.

that the formation of the O58—La1 coordinate bond has little effect on the W7—O58 bond.

In the crystal structure there are C—H...O and O—H...O hydrogen bonds (Table 2). $[\text{La}(\text{DMF})_7(\text{H}_2\text{O})]^{3+}$ cations and POM anions form infinite chains along the *c* axis *via* La—O—W bonds and hydrogen bonds (Fig. 3), while DMP cations and POM anions form infinite chains along the *b* axis *via* hydrogen bonds (Fig. 4). These chains crosslink to form an infinite three-


Figure 3

Chain of $[\text{La}(\text{DMF})_7(\text{H}_2\text{O})]^{3+}$ cations and $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ anions along the *c* axis; displacement ellipsoids are depicted at the 10% probability level. Dashed lines indicate hydrogen bonds.


Figure 4

Chain of DMP cations and $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ anions along the *b* axis; displacement ellipsoids are depicted at the 10% probability level. Dashed lines indicate hydrogen bonds.

dimensional assembly through hydrogen bonds and electrostatic forces. DMP cations are located around POM anions and DMF solvent molecules are dispersed throughout the framework.

Experimental

$\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was prepared according to the literature method (Contant, 1990). 1,4-Dimethylpyridinium iodide (DMPI) was prepared following Ren *et al.* (2000). Compound (I) was prepared by mixing a 0.01 mol l^{-1} LaCl_3/DMF solution, a 0.01 mol l^{-1} DMPI/DMF solution and a 0.01 mol l^{-1} $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}/\text{DMF}$ solution in the molar ratio 1:3:1. Bright-blue crystals of (I) were obtained from the reaction mixture by slow diffusion of water at room temperature. Yield *ca* 10% (evaluated from LaCl_3). Elemental analysis calculated: C 10.47, H 1.74, N 3.05%; found: C 9.83, H 1.67, N 2.57%

Crystal data

(C₇H₁₀N)₃[La(P₂W₁₈O₆₂)-
(C₃H₇NO)₇(H₂O)]·2C₃H₇NO
M_r = 5502.51
 Orthorhombic, *Pna*2₁
a = 38.970 (19) Å
b = 14.804 (7) Å
c = 18.441 (9) Å
V = 10639 (9) Å³

Z = 4
D_x = 3.431 Mg m⁻³
 Mo *K*α radiation
μ = 19.90 mm⁻¹
T = 298 (2) K
 Plate, blue
 0.58 × 0.25 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: part of the refinement model (Δ*F*) (Parkin *et al.*, 1995)
T_{min} = 0.003, *T_{max}* = 0.366

61983 measured reflections
 21381 independent reflections
 15566 reflections with *I* > 2σ(*I*)
R_{int} = 0.091
θ_{max} = 26.8°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.106
wR(*F*²) = 0.262
S = 1.00
 21381 reflections
 1300 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.1368*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 4.97 e Å⁻³
 Δρ_{min} = -4.08 e Å⁻³
 Absolute structure: Flack (1983),
 9699 Friedel pairs
 Flack parameter: 0.02 (1)

Table 1

Selected geometric parameters (Å, °).

La1—O58	2.70 (3)	La1—O74	2.53 (4)
La1—O70	2.53 (4)	La1—O75	2.65 (4)
La1—O71	2.58 (4)	La1—O76	2.49 (3)
La1—O72	2.46 (4)	La1—O77	2.46 (4)
La1—O73	2.57 (4)		
W7—O58—La1	172.9 (17)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
O70—H702···O41 ⁱ	0.85	2.41	2.82 (5)	111
C1—H1···O46 ⁱⁱ	0.93	2.49	3.33 (5)	150
C15—H15···O78 ⁱⁱⁱ	0.93	2.39	3.21 (10)	148
C16—H16B···O49 ⁱⁱⁱ	0.96	2.45	3.30 (6)	148
C21—H21···O33	0.93	2.34	3.26 (7)	171
C22—H22···O49	0.93	2.45	3.33 (7)	158
C24—H24···O31 ^{iv}	0.93	2.45	3.34 (7)	161
C25—H25···O2 ^{iv}	0.93	2.53	3.35 (6)	148
C26—H26C···O60 ^{iv}	0.96	2.30	3.25 (11)	171
C31—H31A···O71	0.96	2.31	2.74 (7)	106
C31—H31C···O31 ^v	0.96	2.49	3.25 (6)	135
C32—H32C···O32 ⁱⁱ	0.96	2.53	3.17 (6)	124
C40—H40···O58	0.93	2.54	3.11 (5)	120
C41—H41A···O72	0.96	2.42	2.80 (6)	103
C41—H41C···O29 ^v	0.96	2.51	3.44 (7)	163
C42—H42A···O31	0.96	2.57	3.32 (9)	135
C51—H51A···O50 ^v	0.96	2.23	3.12 (6)	154

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C51—H51B···O54 ⁱ	0.96	2.58	3.35 (6)	138
C51—H51C···O31 ^v	0.96	2.55	3.42 (6)	150
C52—H52A···O73	0.96	2.24	2.66 (8)	105
C52—H52C···O54 ⁱ	0.96	2.24	3.12 (9)	152
C61—H61B···O61	0.96	2.48	3.14 (9)	126
C62—H62A···O74	0.96	2.33	2.73 (6)	104
C62—H62B···O26 ⁱⁱⁱ	0.96	2.57	3.11 (5)	116
C71—H71A···O75	0.96	2.39	2.80 (7)	105
C71—H71B···O52 ⁱ	0.96	2.47	3.08 (5)	121
C82—H82C···O49	0.96	2.59	3.52 (7)	164
C100—H100···O51 ⁱⁱ	0.93	2.59	3.37 (6)	142
C102—H97A···O78	0.96	2.25	2.66 (8)	104
C102—H97C···O29 ^{vi}	0.96	2.50	3.30 (6)	141
C111—H11A···O16 ^{vii}	0.96	2.49	3.14 (9)	125

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

Because a regularly shaped crystal could not be obtained, and the faces could not be indexed adequately, our attempts to apply a numerical absorption correction were unsuccessful. Multi-scan and reldelf absorption corrections were used as comparison, and the latter can lead to a better result, though the *R* value (0.1057) was still high. Restraints and constraints (ISOR, FLAT, DFIX, SADI and DELU instructions in *SHELXL97*; Sheldrick, 1997) were used in order to maintain a reasonable geometry and atomic displacement parameters for DMP and DMF molecules. The H atoms of the water molecule were positioned with the *CALCOH* instruction (Nardelli, 1999) in *WinGX* (Farrugia, 1999), the O—H distance being 0.82–0.85 Å; *U_{iso}*(H) = 1.5*U_{eq}*(O). All other H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances 0.93–0.96 Å, and with *U_{iso}*(H) = 1.2*U_{eq}*(C) or 1.5*U_{eq}*(C) for methyl groups.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; 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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