$O4^{vii}$—P1—$O2^{iv}$	102,9 (10)	$O10^{ii}$—P3—$O10^{viii}$	105,8 (10)
$O2^{iv}$—P1—O6	106,3 (9)	O11—P3—$O10^{ii}$	108,1 (9)
O8—P1—$O2^{iv}$	116,2 (10)	O11—P3—$O10^{viii}$	108,1 (9)
$O4^{vii}$—P1—O6	114,3 (10)	O13—P3—$O10^{ii}$	108,8 (9)
O8—P1—$O4^{vii}$	108,6 (10)	O13—P3—$O10^{viii}$	108,8 (9)
O8—P1—O6	108,7 (10)	O13—P3—O11	116,7 (10)
$O3^{i}$—P2—$O1^{v}$	102,0 (10)	$O9^{vi}$—P4—$O9^{ix}$	105,9 (13)
O5—P2—$O1^{v}$	102,5 (10)	O12—P4—$O9^{vi}$	112,4 (10)
O7—P2—$O1^{v}$	115,6 (10)	O12—P4—$O9^{ix}$	112,4 (10)
O5—P2—$O3^{i}$	116,4 (10)	$O9^{vi}$—P4—O14	110,8 (9)
O7—P2—$O3^{i}$	107,4 (10)	$O9^{ix}$—P4—O14	110,8 (9)
O5—P2—O7	112,7 (10)	O12—P4—O14	104,6 (15)

Codes de symétrie: (i) $x-1, y, z$; (ii) $x, y, z-1$; (iii) $x-1, y, z-1$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (vi) $x, y, 1+z$; (vii) $1+x, y, z$; (viii) $x, -y, z-1$; (ix) $x, -y, 1+z$.

Collection des données: Rigaku *AFC/MSC Software* (Rigaku Corporation, 1991). Affinement des paramètres de la maille: Rigaku *AFC/MSC Software*. Réduction des données: *TEXSAN* (Molecular Structure Corporation, 1985). Programme(s) pour la solution de la structure: *RSSFR*-5, *UNICS* (Sakurai, 1971) et *TEXSAN* (Molecular Structure Corporation, 1985). Programme(s) pour l'affinement de la structure: *RSFLS*-4, *UNICS*. Graphisme moléculaire: *ORTEP*II (Johnson, 1971) et *ATOMS*2,2 (Dowty, 1992). Logiciel utilisé pour préparer le matériel pour publication: *LISTHKL* (Yamakawa & Kawahara, 1994) et *CCPC* (Kawamura & Kawahara, 1980).

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Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: DU1180). Les processus d'accès à ces archives est donné au dos de la couverture.

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$(NH_4)_3[PMo_{12}O_{40}].21H_2O$

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Abstract

The determination of the crystal structure of the title compound, triammonium hexatriacontaoxo(tetraoxophosphato)dodecamolybdate(3−) henicosahydrate, shows that the polyanion has a pseudo-Keggin structure with $m\bar{3}m$ symmetry. The central PO_4 group is disordered with P—O distances of 1.55 (3) Å. The Mo—O distances range from 1.617 (14) to 2.414 (14) Å.

Comment

The structure of the heteropolyanion $[PMo_{12}O_{40}]^{3-}$ was first reported by Strandberg (1975) and D'amour & Allmann (1976). It is a Keggin-type structure (Keggin, 1934): the PO_4 tetrahedron is at the centre; three MoO_6 octahedra are linked together through shared edges to

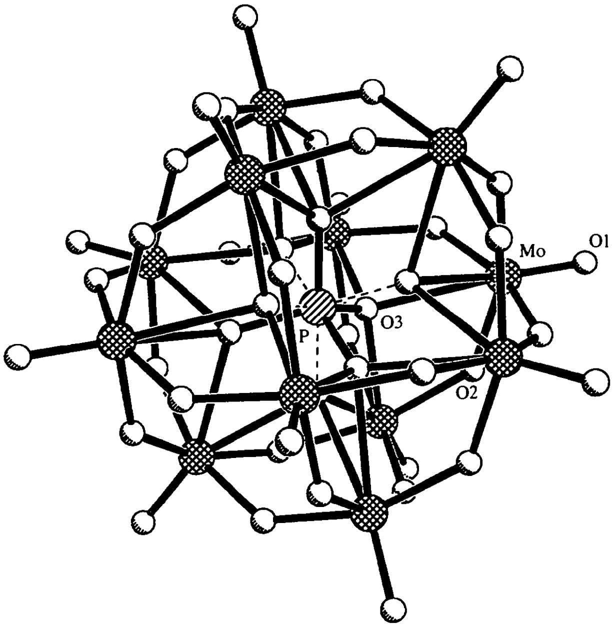

Fig. 1. The structure of the $[PMo_{12}O_{40}]^{3-}$ anion.

form an Mo_3O_{13} unit, the central O atom of which is bonded to P; four Mo_3O_{13} groups complete the Keggin anion. The title compound is a pseudo-Keggin heteropoly compound in which the PO_4 group is disordered (Fig. 1). This kind of structure has been observed in the polyanions $[PMo_{10}V_2O_{40}]^{5-}$ and $[PMo_9V_3O_{40}]^{6-}$ (Sergienko *et al.*, 1980; Shan *et al.*, 1991). The O atoms of the phosphate anion have an occupancy of 0.5 and lie at the corners of a cube. In the title structure, the length of the edge of this cube is 1.79 (3) Å and the P—O distances are 1.55 (3) Å.

The O atoms in the anion can be divided into three groups, O*a*, O*b* and O*t*, where O*t* represents a terminal O atom bound to one Mo atom, O*b* represents a bridging O atom bound to two Mo atoms, and O*a* represents a central O atom; O*a* is disordered. The Mo—O distances are 1.617 (14) (Mo—O*t*), 1.884 (5) (Mo—O*b*) and 2.414 (14) Å (Mo—O*a*). These distances are comparable to those found in similar structures (Sergienko *et al.*, 1980; Shan *et al.*, 1991). The NH_4^+ ions and water molecules fill space in the unit cell.

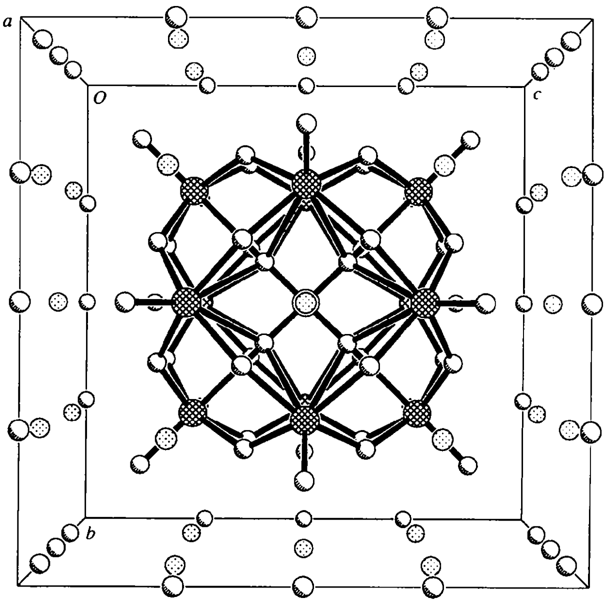

Fig. 2. Packing diagram viewed down the *a* axis. N atoms are at the face centres and water O atoms are represented by open or stippled circles on the cell faces. Other atoms are as depicted in Fig. 1.

Experimental

The compound was prepared by hydrothermal synthesis from NH_4VO_3 and Na_2MoO_4 in aqueous solution by adding phosphorus acid (pH = 4.0). After cooling the solution to room temperature, dark-green single crystals suitable for X-ray diffraction studies were obtained.

Crystal data

$(NH_4)_3[PMo_{12}O_{40}].21H_2O$
$M_r = 2254.66$
Cubic
$Pm\bar{3}m$
$a = 10.940 (1)$ Å
$V = 1309.4 (3)$ Å^3
$Z = 1$
$D_x = 2.862$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 5.26$–$12.42°$
$\mu = 2.939$ mm^{-1}
$T = 293 (2)$ K
Cube
0.26 × 0.24 × 0.24 mm
Dark green

Data collection

Siemens *P*4 diffractometer
ω–2θ scans
Absorption correction: empirical *via* ψ scans (North *et al.*, 1968)
$T_{min} = 0.229$, $T_{max} = 0.382$
1875 measured reflections
280 independent reflections
266 reflections with $I > 2\sigma(I)$

$R_{int} = 0.096$
$\theta_{max} = 25°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 12$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.139$
$S = 1.267$
280 reflections
29 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2 + 18.2820P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 2.02$ e Å^{-3}
$\Delta\rho_{min} = -1.76$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0015 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Mo	0.27332 (8)	1/2	*x*	0.0254 (7)
P	1/2	1/2	1/2	0.027 (3)
O1	0.1688 (9)	1/2	*x*	0.073 (5)
O2	0.3806 (9)	*x*	0.2108 (12)	0.087 (5)
O3†	0.4182 (14)	*x*	*x*	0.029 (6)
N1	1/2	1/2	0	0.089 (16)
O*W*1	0.258 (2)	*x*	0	0.114 (11)
O*W*2	0	1/2	0	0.24 (4)
O*W*3	0	0.273 (7)	0	0.36 (6)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Mo—O1	1.617 (14)	Mo—O2^{iii}	1.884 (5)
Mo—O2^{i}	1.884 (5)	Mo—O3	2.414 (14)
Mo—O2	1.884 (5)	P—O3	1.55 (3)
Mo—O2^{ii}	1.884 (5)		
O1—Mo—O2	100.6 (4)	O2—Mo—O3	64.7 (5)
O1—Mo—O3	158.2 (5)	O3—P—O3^{iv}	109.5

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

The highest peak in the difference map is 0.84 Å from O*W*1 and 1.65 Å from O*W*3, and the largest hole is 0.875 Å from O*W*1.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1160). Services for accessing these data are described at the back of the journal.

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$LaAl_{2.03}(B_4O_{10})O_{0.54}$

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Abstract

The title compound, lanthanum aluminium borate, has been found to be isostructural with hexagonal $NdAl_{2.07}(B_4O_{10})O_{0.6}$. Each La ion is coordinated by six O atoms to form a trigonal prism, while each Al is coordinated by five O atoms to form a pyramid.

Comment

The structure determination of the title compound was carried out as part of a sequence of research on $MAl_3(BO_3)_4$ (M = La, Sm, Gd, Nd) materials. The compound is non-stoichiometric. The structure is different from the rhombohedral structure of the $NdAl_3(BO_3)_4$ family (Hong & Dwight, 1974), but similar to that of $NdAl_{2.07}(B_4O_{10})O_{0.6}$ (Pushcharovskii *et al.*, 1978). The La, Al and B atoms are surrounded by O atoms in trigonal prismatic, pyramidal and tetrahedral arrangements, respectively. The BO_4 tetrahedra distinguish this structure from that of the $NdAl_3(BO_3)_4$ family, where the BO_3 units are planar. BO_4 tetrahedra share corners to form a net parallel to the *ab* plane; the other polyhedra share corners and edges.

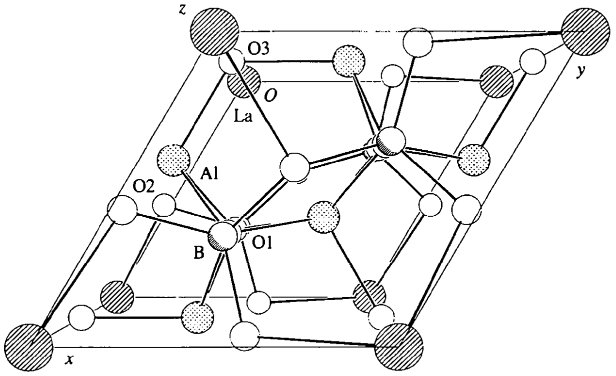

Fig. 1. Projection of the structure of the title compound on the *ab* plane.

Experimental

The title compound was prepared by heating a mixture of La_2O_3 and Al_2O_3 over B_2O_3, with PbF_2 and PbO as stabilizers, in a platinum crucible at 1323 K for 12 h (Wei, Jiang & Liu, 1993). The crucible was cooled slowly to room temperature, yielding single crystals.

Crystal data

$LaAl_{2.03}B_4O_{10.54}$
$M_r = 405.55$
Hexagonal
$P\bar{6}2m$
$a = 4.606\,(1)$ Å
$c = 9.348\,(2)$ Å
$V = 171.75\,(6)$ Å^3
$Z = 1$
$D_x = 3.921$ Mg m^{-3}
$D_m = 3.94\,(1)$ Mg m^{-3}
D_m measured by flotation in H_2O
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3$–$13°$
$\mu = 6.547$ mm^{-1}
$T = 295$ K
Prism
0.20 × 0.10 × 0.06 mm
Colourless

Data collection

Nicolet $R3m/E$ diffractometer
$\theta/2\theta$ scans
407 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$

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