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Aluminium cyclohexaphosphate

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Key indicators: single-crystal X-ray study; T = 296 K; mean σ(P–O) = 0.003 Å; R factor = 0.032; wR factor = 0.130; data-to-parameter ratio = 14.2.

Single crystals of the title compound, $Al_2P_6O_{18}$, were obtained by solid-state reaction. The monoclinic structure is isotypic with its Cr^{III}, Ga^{III} and Ru^{III} analogues and is built up of six-membered phosphate ring anions, $P_6O_{18}{}^{6-}$, isolated from each other and further linked by isolated AlO_6 octahedra by sharing corners. Each AlO_6 octahedron is linked to four $P_6O_{18}{}^{6-}$ rings. More accurately, two rings are linked through bidentate diphosphate groups attached in the *cis*-positions to the AlO_6 octahedron. The other two rings are linked to the two remaining corners, also in *cis*-positions of the AlO_6 octahedron.

Related literature

The title compound was first synthesized by Kanene *et al.* (1985) and its unit cell determined from Weissenberg photographs. Isotypic compounds have been reported: $Ga_2P_6O_{18}$ (Chudinova *et al.*, 1987); $Cr_2P_6O_{18}$ (Bagieu-Beucher & Guitel, 1977) and $Ru_2P_6O_{18}$ (Fukuoka *et al.*, 1995). For a review of the crystal chemistry of cyclohexaphosphates, see: Durif (1995, 2005). For applications of aluminium phosphate, see: Vippola *et al.* (2000). For the structures of other cyclohexaphosphates with the $P_6O_{18}{}^{6-}$ anion, see: Averbuch-Pouchot & Durif (1991*a*,*b*,*c*).

Experimental

Crystal data

$Al_2P_6O_{18}$
M_r = 527.79
Monoclinic, $P2_1/c$
a = 6.0931 (2) Å
b = 15.0676 (4) Å
c = 8.2016 (3) Å
β = 105.166 (1)°
V = 726.75 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 296 K
0.16 × 0.07 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008) T_{min} = 0.860, T_{max} = 0.945
6548 measured reflections
1674 independent reflections
1398 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.130
S = 1.16
1674 reflections
118 parameters
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.471 (2)	P3—O2	1.479 (3)
P1—O5	1.478 (2)	P3—O9^{ii}	1.594 (2)
P1—O7	1.587 (2)	P3—O8^{iii}	1.597 (2)
P1—O9	1.594 (3)	Al—O3	1.852 (2)
P2—O4	1.482 (2)	Al—O2^{iv}	1.873 (3)
P2—O6	1.487 (2)	Al—O1	1.877 (3)
P2—O7^{i}	1.579 (2)	Al—O4	1.887 (3)
P2—O8	1.593 (2)	Al—O5^{v}	1.889 (3)
P3—O1	1.476 (2)	Al—O6^{iii}	1.904 (2)
P2^{v}—O7—P1	139.91 (16)	P1—O9—P3^{vi}	129.42 (16)
P2—O8—P3^{iii}	130.56 (16)		

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

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: CaRine (Boudias & Monceau, 1998) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2303).

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supplementary materials

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Aluminium cyclohexaphosphate

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Comment

Although the $Al_2P_60_{18}$ cyclohexaphosphate is known since twenty five years (Kanene *et al.*, 1985), its crystal structure has never been refined from single crystal X-ray diffraction data. This paper deals with this purpose.

The crystal structure of $Al_2P_60_{18}$ is isotypic with $Cr_2P_6O_{18}$ (Bagieu-Beucher & Guitel, 1977), $Ga_2P_6O_{18}$ (Chudinova *et al.*, 1987) and $Ru_2P_6O_{18}$ (Fukuoka *et al.*, 1995). It is built up of six-membered phosphate ring anions $(P_6O_{18})^{6-}$ isolated from each others and further linked by AlO_6 octahedra by sharing corners. These centrosymmetric ring anions $(P_6O_{18})^{6-}$ are located around inversion centers at 0 0 1/2 and 0 1/2 0 (Fig. 1a). Their mean planes are parallel to either $(\overline{1}\overline{2}1)$ or $(1\overline{2}\overline{1})$ planes (Fig. 1 b). Each AlO_6 octahedron is linked to four P_6O_{18} rings. More accurately, two rings are linked through bidentate diphosphate groups attached in *cis*-positions to the AlO_6 octahedron. The two other rings are linked to the two remaining corners of the AlO_6 octahedron (Fig. 2). Each $(P_6O_{18})^{6-}$ ring anion is connected to eight AlO_6 octahedra by corner-sharing. Four diphosphate groups of the ring anion including $P(3)O_4$ and either $P(1)O_4$ or $P(2)O_4$ tetrahedra are bidentate whereas the $P(1)O_4$—$P(2)O_4$ couple does not bind in a bidentate fashion. This may be correlated with the value of the P(1)—O—P(2) angle (139.91 (16)°) which is greater than P(2)—O—P(3) (130.56 (16)°) and P(1)—O—P(3) (129.42 (16) °) ones and also to the P(1)—P(2) distance (2.9741 (12) Å) slightly greater than P(2)—P(3) = 2.8970 (11) Å and P(1)—P(3) = 2.8826 (12) Å ones.

A survey of the internal symmetry of the $(P_6O_{18})^{6-}$ ring anions shows that most of them are centrosymmetric with P—P—P angles spreading from 87.8° to 142.8° (Averbuch-Pouchot & Durif, 1991*a*), i.e. with large deviations from the ideal value of 120°. When the $(P_6O_{18})^{6-}$ ring anion has internal $\overline{1}$ symmetry, it is built up of three independent P atoms and hence there are three characteristic α_i = P—P—P angles in the ring ($\alpha_1 = P_1—P_2—P_3$, $\alpha_2 = P_2—P_3—P_1$, $\alpha_3 = P_3—P_1—P_2$). When taking the $\delta = \Sigma_i|120-\alpha_i|$ parameter as a rough measure of the ring distorsion, $Al_2P_6O_{18}$ exhibits the third lowest δ = 15.28° value after its homologous congeners $Ru_2P_6O_{18}$ (δ = 13.78°) and $Cr_2P_6O_{18}$ (δ = 14.39°). It should be noted that the characteristic P—P—P angles for both isotypic $Ga_2P_6O_{18}$ and $Fe_2P_6O_{18}$ structures have not been reported. The highest δ values calculated from data for other cyclohexaphosphates reported up to date are related to $Cu_2(NH_4)_2P_6O_{18}\cdot 8H_2O$ (δ = 65.98°) (Averbuch-Pouchot & Durif, 1991*b*) and $Ag_4Li_2P_6O_{18}.2H_2O$ (δ = 67.29°) (Averbuch-Pouchot & Durif, 1991*c*).

For applications of aluminium phosphate, see: Vippola *et al.* (2000). For general reviews on the crystal chemistry of cyclohexaphosphates, see: Durif (1995) and Durif (2005).

Experimental

Single crystals of the title compound have been obtained by reacting Al_2O_3 with $(NH_4)H_2PO_4$ in an alumina boat. A mixture of these reagents in the molar ratio 1:6 was used for the synthesis. The mixture was first heated at 473 K for 24 h. Afterwards the temperature was successively raised to 573 K for 12 h, then to 673 K for 12 additional hours and finally to 923 K. After a heating period of 48 h at this temperature, the sample was cooled to room temperature by switching the furnace off. Translucent rhombs of $Al_2P_6O_{18}$ were extracted from the batch.

Refinement

The highest residual peak in the final difference Fourier map was located 0.47 Å from atom O7 and the deepest hole was located 1.12 Å from atom P3.

Figures

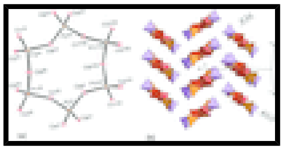

Fig. 1. (a) *ORTEP-3* view of the centrosymmetric $(P_6O_{18})^{6-}$ ring anion. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (iii) 2 - x, 1/2 + y, 1/2 - z; (iv) 1 - x, 1 - y, -z; (v) 2 - x, 1 - y, 1 - z; (vi) x, 1 + y, z; (vii) 1 + x, 1 + y, 1 + z; (viii) x, 3/2 - y, 1/2 + z. (b) Partial projection along [101] showing the orientation of the mean planes of the $(P_6O_{18})^{6-}$ ring anions.

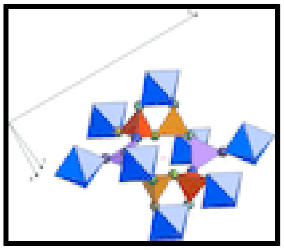

Fig. 2. Partial projection showing the connection between the $(P_6O_{18})^{6-}$ ring anion and the AlO_6 octahedra.

Aluminium hexacyclophosphate

Crystal data

$Al_2P_6O_{18}$	$F(000) = 520$
$M_r = 527.79$	$D_x = 2.412$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2041 reflections
$a = 6.0931$ (2) Å	$\theta = 3.5–27.5°$
$b = 15.0676$ (4) Å	$\mu = 0.96$ mm^{-1}
$c = 8.2016$ (3) Å	$T = 296$ K
$\beta = 105.166$ (1)°	Rhombic, colourless
$V = 726.75$ (4) Å^3	0.16 × 0.07 × 0.06 mm
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	1674 independent reflections
Radiation source: fine-focus sealed tube	1398 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.035$
Detector resolution: 8.3333 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.7°$
φ and ω scans	$h = -7\rightarrow7$

Absorption correction: multi-scan (SADABS; Bruker, 2008)	$k = -11 \rightarrow 19$
$T_{\min} = 0.860$, $T_{\max} = 0.945$	$l = -10 \rightarrow 10$
6548 measured reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.032$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.130$	$w = 1/[\sigma^2(F_o^2) + (0.0787P)^2 + 0.2264P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{\max} < 0.001$
1674 reflections	$\Delta\rho_{\max} = 0.56$ e Å^{-3}
118 parameters	$\Delta\rho_{\min} = -0.71$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
P1	0.70149 (15)	0.33738 (5)	0.01706 (11)	0.0049 (2)
P2	0.64525 (14)	0.04431 (5)	0.21869 (11)	0.0050 (2)
P3	0.08497 (14)	0.11301 (5)	−0.20937 (11)	0.0054 (2)
Al	0.61549 (17)	0.13831 (6)	−0.12313 (13)	0.0046 (3)
O1	0.3051 (4)	0.15855 (15)	−0.1454 (3)	0.0082 (5)
O2	−0.0766 (4)	0.11484 (16)	−0.1026 (3)	0.0090 (5)
O3	0.6755 (4)	0.25850 (15)	−0.0920 (3)	0.0078 (5)
O4	0.6653 (4)	0.12162 (15)	0.1117 (3)	0.0076 (5)
O5	0.5656 (4)	0.34555 (16)	0.1415 (3)	0.0084 (5)
O6	0.4448 (4)	−0.01495 (15)	0.1608 (3)	0.0073 (5)
O7	0.6509 (5)	0.42395 (15)	−0.0967 (3)	0.0109 (5)
O8	0.8737 (4)	−0.01227 (15)	0.2539 (3)	0.0110 (5)
O9	0.9653 (4)	0.34779 (16)	0.1085 (3)	0.0107 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0052 (5)	0.0050 (4)	0.0042 (5)	−0.0007 (3)	0.0008 (3)	0.0001 (3)
P2	0.0060 (5)	0.0041 (4)	0.0050 (5)	−0.0003 (3)	0.0014 (3)	−0.0009 (3)
P3	0.0036 (5)	0.0058 (4)	0.0069 (5)	0.0007 (3)	0.0015 (3)	0.0002 (3)
Al	0.0034 (5)	0.0055 (5)	0.0052 (5)	−0.0006 (4)	0.0015 (4)	−0.0003 (3)
O1	0.0045 (12)	0.0065 (12)	0.0136 (13)	−0.0012 (9)	0.0025 (10)	−0.0021 (9)
O2	0.0050 (12)	0.0127 (12)	0.0094 (13)	−0.0002 (9)	0.0024 (10)	0.0014 (10)
O3	0.0110 (13)	0.0045 (11)	0.0077 (12)	−0.0028 (9)	0.0020 (10)	−0.0015 (9)
O4	0.0119 (13)	0.0059 (11)	0.0053 (12)	−0.0022 (9)	0.0025 (10)	−0.0007 (9)
O5	0.0066 (13)	0.0132 (12)	0.0057 (12)	0.0000 (9)	0.0020 (10)	0.0003 (9)
O6	0.0060 (12)	0.0063 (12)	0.0098 (12)	0.0002 (9)	0.0025 (10)	−0.0012 (9)
O7	0.0221 (15)	0.0059 (12)	0.0053 (12)	0.0033 (9)	0.0045 (11)	0.0022 (9)
O8	0.0061 (12)	0.0073 (12)	0.0175 (14)	−0.0004 (9)	−0.0007 (10)	−0.0038 (9)
O9	0.0052 (13)	0.0186 (13)	0.0084 (13)	−0.0021 (10)	0.0019 (10)	−0.0062 (10)

Geometric parameters (Å, °)

P1—O3	1.471 (2)	Al—O3	1.852 (2)
P1—O5	1.478 (2)	Al—O2^{iv}	1.873 (3)
P1—O7	1.587 (2)	Al—O1	1.877 (3)
P1—O9	1.594 (3)	Al—O4	1.887 (3)
P2—O4	1.482 (2)	Al—O5^{v}	1.889 (3)
P2—O6	1.487 (2)	Al—O6^{iii}	1.904 (2)
P2—O7^{i}	1.579 (2)	O2—Al^{vi}	1.873 (3)
P2—O8	1.593 (2)	O5—Al^{i}	1.889 (3)
P3—O1	1.476 (2)	O6—Al^{iii}	1.904 (2)
P3—O2	1.479 (3)	O7—P2^{v}	1.579 (2)
P3—O9^{ii}	1.594 (2)	O8—P3^{iii}	1.597 (2)
P3—O8^{iii}	1.597 (2)	O9—P3^{vii}	1.594 (3)
O3—P1—O5	119.77 (14)	O3—Al—O4	90.93 (11)
O3—P1—O7	109.47 (14)	O2^{iv}—Al—O4	89.61 (11)
O5—P1—O7	106.27 (14)	O1—Al—O4	90.56 (12)
O3—P1—O9	107.50 (14)	O3—Al—O5^{v}	89.33 (11)
O5—P1—O9	110.17 (14)	O2^{iv}—Al—O5^{v}	90.32 (11)
O7—P1—O9	102.27 (14)	O1—Al—O5^{v}	89.50 (11)
O4—P2—O6	118.09 (14)	O4—Al—O5^{v}	179.74 (12)
O4—P2—O7^{i}	110.17 (13)	O3—Al—O6^{iii}	178.54 (12)
O6—P2—O7^{i}	107.36 (14)	O2^{iv}—Al—O6^{iii}	88.66 (11)
O4—P2—O8	108.93 (14)	O1—Al—O6^{iii}	89.77 (11)
O6—P2—O8	110.01 (13)	O4—Al—O6^{iii}	90.46 (11)
O7^{i}—P2—O8	100.91 (14)	O5^{v}—Al—O6^{iii}	89.29 (11)
O1—P3—O2	117.68 (15)	P3—O1—Al	139.30 (16)

O1—P3—O9^{ii}	108.14 (14)	P3—O2—Al^{vi}	139.15 (17)
O2—P3—O9^{ii}	109.62 (14)	P1—O3—Al	149.33 (16)
O1—P3—O8^{iii}	109.89 (14)	P2—O4—Al	133.84 (15)
O2—P3—O8^{iii}	108.82 (14)	P1—O5—Al^{i}	138.32 (16)
O9^{ii}—P3—O8^{iii}	101.47 (14)	P2—O6—Al^{iii}	138.20 (15)
O3—Al—O2^{iv}	90.88 (11)	P2^{v}—O7—P1	139.91 (16)
O3—Al—O1	90.69 (11)	P2—O8—P3^{iii}	130.56 (16)
O2^{iv}—Al—O1	178.43 (11)	P1—O9—P3^{vii}	129.42 (16)

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) *x*−1, −*y*+1/2, *z*−1/2; (iii) −*x*+1, −*y*, −*z*; (iv) *x*+1, *y*, *z*; (v) *x*, −*y*+1/2, *z*−1/2; (vi) *x*−1, *y*, *z*; (vii) *x*+1, −*y*+1/2, *z*+1/2.

Fig. 1

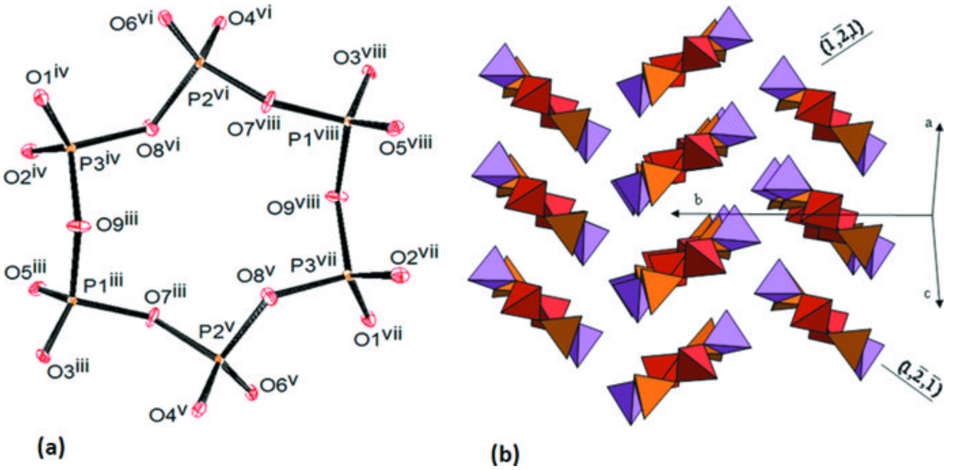
O6vi
O4vi
O1iv
P2vi
O3viii
O7viii
P1viii
O5viii
O8vi
P3iv
O2iv
O9iii
O9viii
O5iii
P1iii
O8v
P3vii
O2vii
O7iii
P2v
O1vii
O3iii
O6v
O4v
(a)
(1̄,2̄,1)
a
b
c
(1,2̄,1̄)
(b)

Fig. 2