

Crystal structure of AlPCl_8

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The crystal structure of aluminium phosphorus chloride (systematic name: phosphorus tetrachloride tetrachloridoaluminate), $(\text{PCl}_4)[\text{AlCl}_4]$ or AlPCl_8 , was determined and refined using single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic space group $Pbcm$. The asymmetric unit comprises one Al atom, one P atom, and five Cl atoms. The structure is characterized by isolated AlCl_4 and PCl_4 tetrahedra, isostructural with FePCl_8 and GaPCl_8 .

1. Chemical context

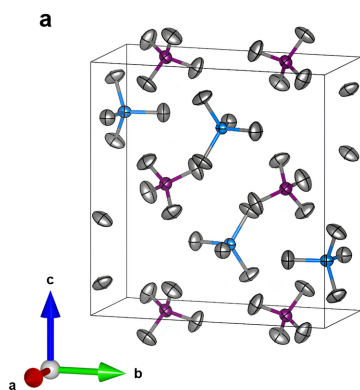
During our exploratory synthesis in the Mg–Al–P–Cl system, aimed at discovering new magnesium-ion conductors, we initially observed the AlPCl_8 phase. Magnesium-ion conductors, such as MgAl_2Cl_8 , exhibit Mg-ion conductivity of approximately $10^{-7} \text{ S cm}^{-1}$ at 400 K (Tomita *et al.*, 2021). To enhance this ionic conductivity, we introduced an aliovalent substitution of Al with P to create magnesium-ion vacancies within the structure, following the general formula $\text{Mg}_{1-x}\text{Al}_{2-x}\text{P}_x\text{Cl}_8$.

Across a wide range of x values (0.1 to 1), we identified a new phase through powder X-ray diffraction (XRD) patterns, which differed significantly from that of MgAl_2Cl_8 . Subsequent analysis revealed that this new phase matched the XRD pattern of AlPCl_8 (Fischer & Jübermann, 1938). Since the crystal structure of AlPCl_8 was previously unknown, we proceeded to grow single crystals without Mg to determine its structure. The resulting analysis confirmed that its crystal structure is isostructural with FePCl_8 (Kistenmacher & Stucky, 1968) and GaPCl_8 (Weigand *et al.*, 2009).

2. Structural commentary

Anhydrous aluminium phosphorus chloride (AlPCl_8) crystallizes in the orthorhombic space group $Pbcm$ (Fig. 1), with a structure consisting of isolated AlCl_4 and PCl_4 tetrahedra, and one Al, one P, and five Cl sites in the asymmetric unit. Al^{3+} is tetrahedrally coordinated by four Cl atoms, with an average Al–Cl bond distance of 2.127 (2) Å, while P^{5+} is similarly coordinated, but a shorter average P–Cl bond distance of 1.899 (2) Å. These bond lengths (Table 1) are consistent with the sums of the ionic radii for Al, P, and Cl (Shannon, 1976). The local environment of each tetrahedron is shown in Fig. 2. The crystal structure was determined to be isostructural with $(\text{FeCl}_4)(\text{PCl}_4)$ (Kistenmacher & Stucky, 1968).

To validate the refined crystal structure, bond-valence sums (BVSs) were calculated using the *softBV* (Chen *et al.*, 2019) program (V1.3.1). The calculated BVS values closely match



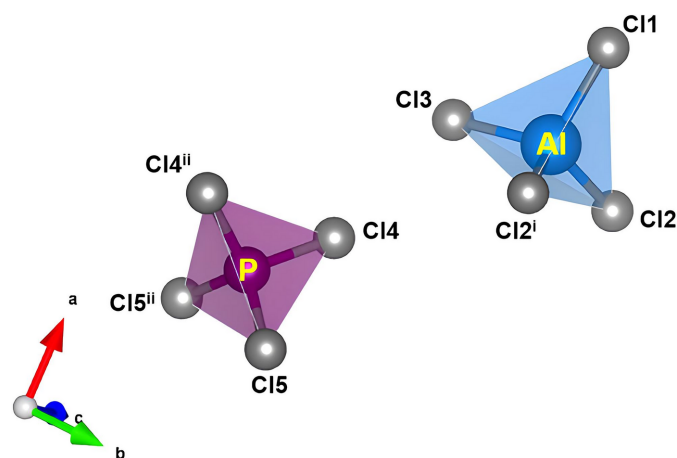


Figure 1
The local environments of the AlCl_4 (blue) and PCl_4 tetrahedra (purple) are shown. Symmetry codes correspond to those in Table 1.

the expected ionic charges, further supporting the reliability of the structural model: Al 3.04, P 5.05, Cl1 – 0.77, Cl2 – 0.78, Cl3 – 0.78, Cl4 – 1.25, and Cl5 – 1.24.

3. Synthesis and crystallization

Anhydrous aluminium chloride (AlCl_3 , Alfa Aesar, anhydrous, reagent grade) and phosphorus(V) chloride (PCl_5 , Sigma-Aldrich, 95%) were used in the experiment. A stoichiometric mixture of AlCl_3 and PCl_5 was ground using a mortar and pestle and then pressed into a pellet. The pellet was placed in a dry fused-silica ampoule, which was sealed under vacuum and heated in a furnace. The temperature was increased from 303 K to 573 K at a rate of 5 K min^{-1} , then gradually lowered to 373 K at a rate of $0.0694 \text{ K min}^{-1}$. The sample was then allowed to cool naturally to room temperature. Single crystals were collected at 293 K using an optical microscope in a dry room with a dew point of 223 K. A crystal,

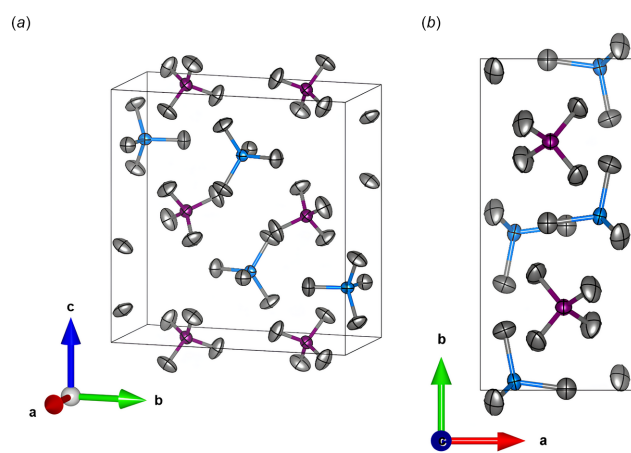


Figure 2
The displacement of ellipsoids of AlPCl_8 drawn at the 50% probability level viewed from two different orientations: (a) approximately along the [111] direction and (b) along the [001] direction. The AlCl_4 tetrahedra are represented in blue, and the PCl_4 tetrahedra in purple.

Table 1
Selected geometric parameters (\AA , $^\circ$).

$\text{Al1} - \text{Cl2}^{\text{i}}$	2.1223 (12)	$\text{P1} - \text{Cl5}^{\text{ii}}$	1.9018 (12)
$\text{Al1} - \text{Cl1}$	2.1343 (16)	$\text{P1} - \text{Cl4}^{\text{ii}}$	1.8959 (12)
$\text{Al1} - \text{Cl2}$	2.1223 (12)	$\text{P1} - \text{Cl4}$	1.8959 (12)
$\text{Al1} - \text{Cl3}$	2.128 (2)	$\text{P1} - \text{Cl5}$	1.9018 (12)
$\text{Cl2}^{\text{i}} - \text{Al1} - \text{Cl1}$	108.79 (6)	$\text{Cl5}^{\text{ii}} - \text{P1} - \text{Cl4}^{\text{ii}}$	109.31 (6)
$\text{Cl2}^{\text{i}} - \text{Al1} - \text{Cl2}$	112.83 (10)	$\text{Cl5}^{\text{ii}} - \text{P1} - \text{Cl4}$	110.49 (6)
$\text{Cl1} - \text{Al1} - \text{Cl2}$	108.79 (6)	$\text{Cl4}^{\text{ii}} - \text{P1} - \text{Cl4}$	108.26 (9)
$\text{Cl2}^{\text{i}} - \text{Al1} - \text{Cl3}$	108.77 (6)	$\text{Cl5}^{\text{ii}} - \text{P1} - \text{Cl5}$	108.97 (8)
$\text{Cl1} - \text{Al1} - \text{Cl3}$	108.82 (8)	$\text{Cl4}^{\text{ii}} - \text{P1} - \text{Cl5}$	110.49 (6)
$\text{Cl2} - \text{Al1} - \text{Cl3}$	108.77 (6)	$\text{Cl4} - \text{P1} - \text{Cl5}$	109.31 (6)

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

approximately 0.1 mm in size, was placed into a 0.5 mm diameter glass capillary and sealed with capillary wax (Hampton Research). The same sample was subsequently used for powder analysis.

4. Refinement

Details of the data collection and structure refinement are summarized in Table 2. Single-crystal X-ray diffraction data for AlPCl_8 were collected and processed using *APEX2* (Bruker, 2006), with absorption corrections applied through *SAINT* (Bruker, 2006). The structure was solved using *SUPERFLIP* (Palatinus & Chapuis, 2007) and refined using *CRYSTALS* (Betteridge *et al.*, 2003). Three-dimensional Fourier electron-density maps were visualized using *MCE* (Rohlíček & Hušák, 2007), and structural visualizations were generated using *VESTA* (Momma & Izumi, 2011).

Table 2
Experimental details.

Crystal data	$\text{PCl}_4^+ \cdot \text{AlCl}_4^-$
Chemical formula	341.55
M_r	Orthorhombic, <i>Pbcm</i>
Crystal system, space group	293
Temperature (K)	6.2653 (6), 13.5033 (12), 14.0112 (13)
a, b, c (\AA)	1185.38 (19)
V (\AA^3)	4
Z	Mo $K\alpha$
Radiation type	2.05
μ (mm^{-1})	0.2 × 0.2 × 0.2
Crystal size (mm)	
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
$T_{\text{min}}, T_{\text{max}}$	0.664, 0.671
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	38491, 1399, 1061
R_{int}	0.130
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.647
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.093, 0.056, 1.17
No. of reflections	1061
No. of parameters	51
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.79, –1.04

Computer programs: *APEX2* and *SAINT* (Bruker, 2006), *SUPERFLIP* (Palatinus & Chapuis, 2007), *CRYSTALS* (Betteridge *et al.*, 2003) and *VESTA* (Momma & Izumi, 2011).

The structure of AlPCl_8 was further confirmed using the powder X-ray Rietveld refinement technique. Data were collected with a Bruker AXS D8 Advance powder X-ray diffractometer, equipped with $\text{Cu } K\alpha_1$ radiation in Debye-Scherrer geometry, a focusing primary Ge (111) monochromator, and a Vantec position-sensitive detector with a 6° detector slit. The powder sample was homogeneously mixed with carbon (Super C, TIMCAL) at a 1:1 weight ratio to reduce preferred orientation effects, lower effective packing density, and mitigate absorption effects. The sample was placed in a 0.5 mm glass capillary and sealed with wax to prevent air exposure. Measurements were taken over an angular range of $10^\circ \leq 2\theta \leq 130^\circ$, with a step size of 0.016693° , conducted over 13 h at room temperature. Powder profile refinement was performed using *GSAS-II* software (Toby & Von Dreele, 2013). The final Rietveld plot is shown in Fig. 3.

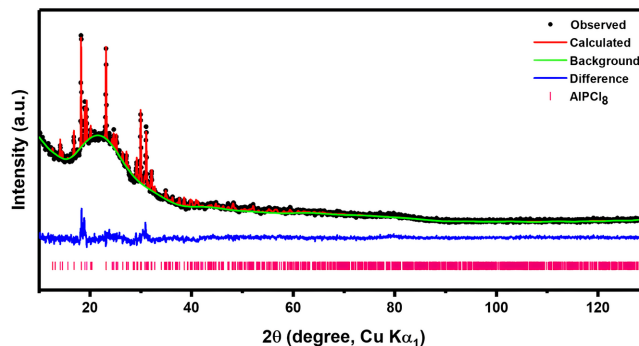


Figure 3
Powder X-ray Rietveld refinement profile of AlPCl_8 . Black dots indicate the observed pattern, the red line represents the calculated pattern, the blue line shows the difference between the observed and calculated patterns, and the pink tick marks correspond to the Bragg reflections positions.

Funding information

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Computing details

Phosphorus tetrachloride tetrachloridoaluminate

Crystal data

$\text{PCl}_4^+ \cdot \text{AlCl}_4^-$

$M_r = 341.55$

Orthorhombic, *Pbcm*

Hall symbol: -P 2c 2b

$a = 6.2653$ (6) Å

$b = 13.5033$ (12) Å

$c = 14.0112$ (13) Å

$V = 1185.38$ (19) Å³

$Z = 4$

$F(000) = 656$

$D_x = 1.914$ Mg m⁻³

$D_m = 1.914$ Mg m⁻³

D_m measured by not measured

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 38491 reflections

$\theta = 3.4$ – 27.4°

$\mu = 2.05$ mm⁻¹

$T = 293$ K

Block, white

$0.2 \times 0.2 \times 0.2$ mm

Data collection

Bruker D8 Venture

diffractometer

Graphite monochromator

$\omega/2\theta$ scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.664$, $T_{\max} = 0.671$

38491 measured reflections

1399 independent reflections

1061 reflections with $I > 2.0\sigma(I)$

$R_{\text{int}} = 0.130$

$\theta_{\max} = 27.4^\circ$, $\theta_{\min} = 3.0^\circ$

$h = -8 \rightarrow 8$

$k = -17 \rightarrow 17$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.093$

$wR(F^2) = 0.056$

$S = 1.17$

1061 reflections

51 parameters

0 restraints

Primary atom site location: other

Weighting scheme based on measured s.u.'s

Method = SQRT(W) = 1/(Data with the key

SIGMA(/FO/) in list 6)

$(\Delta/\sigma)_{\max} = 0.0003$

$\Delta\rho_{\max} = 0.79$ e Å⁻³

$\Delta\rho_{\min} = -1.04$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Al1	0.2214 (2)	0.47461 (11)	0.2500	0.0427
P1	0.45745 (17)	0.7500	0.5000	0.0479
Cl1	0.55881 (16)	0.49641 (12)	0.2500	0.0638

Cl2	0.09231 (14)	0.53762 (10)	0.37618 (9)	0.0859
Cl3	0.1572 (3)	0.31987 (12)	0.2500	0.0839
Cl4	0.28015 (19)	0.80367 (9)	0.40331 (8)	0.0952
Cl5	0.63379 (17)	0.85187 (8)	0.55069 (10)	0.0984

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0338 (6)	0.0499 (9)	0.0445 (8)	-0.0005 (6)	0.0000	0.0000
P1	0.0443 (6)	0.0493 (7)	0.0501 (7)	0.0000	0.0000	0.0041 (7)
Cl1	0.0288 (6)	0.0861 (10)	0.0764 (8)	-0.0026 (6)	0.0000	0.0000
Cl2	0.0579 (6)	0.1250 (12)	0.0746 (7)	-0.0020 (5)	0.0154 (5)	-0.0428 (8)
Cl3	0.0807 (10)	0.0571 (9)	0.1140 (13)	-0.0146 (8)	0.0000	0.0000
Cl4	0.0936 (9)	0.1129 (12)	0.0791 (9)	0.0081 (7)	-0.0211 (7)	0.0365 (7)
Cl5	0.0842 (8)	0.0780 (9)	0.1329 (12)	-0.0163 (7)	-0.0074 (6)	-0.0404 (7)

Geometric parameters (Å, °)

Al1—Cl2 ⁱ	2.1223 (12)	P1—Cl5 ⁱⁱ	1.9018 (12)
Al1—Cl1	2.1343 (16)	P1—Cl4 ⁱⁱ	1.8959 (12)
Al1—Cl2	2.1223 (12)	P1—Cl4	1.8959 (12)
Al1—Cl3	2.128 (2)	P1—Cl5	1.9018 (12)
Cl2 ⁱ —Al1—Cl1	108.79 (6)	Cl5 ⁱⁱ —P1—Cl4 ⁱⁱ	109.31 (6)
Cl2 ⁱ —Al1—Cl2	112.83 (10)	Cl5 ⁱⁱ —P1—Cl4	110.49 (6)
Cl1—Al1—Cl2	108.79 (6)	Cl4 ⁱⁱ —P1—Cl4	108.26 (9)
Cl2 ⁱ —Al1—Cl3	108.77 (6)	Cl5 ⁱⁱ —P1—Cl5	108.97 (8)
Cl1—Al1—Cl3	108.82 (8)	Cl4 ⁱⁱ —P1—Cl5	110.49 (6)
Cl2—Al1—Cl3	108.77 (6)	Cl4—P1—Cl5	109.31 (6)

Symmetry codes: (i) $x, y, -z+1/2$; (ii) $x, -y+3/2, -z+1$.