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Crystal structure of $AlPCl_8$

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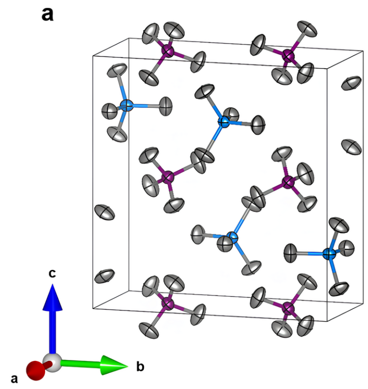
The crystal structure of aluminium phosphorus chloride (systematic name: phosphorus tetrachloride tetrachloridoaluminate), $(PCl_4)[AlCl_4]$ or $AlPCl_8$, was determined and refined using single-crystal X-ray diffraction data. The compound crystallizes in the orthorhombic space group *Pbcm*. The asymmetric 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} 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 $Mg_{1-x}Al_{2-x}P_xCl_8$.

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 $(FeCl_4)(PCl_4)$ (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

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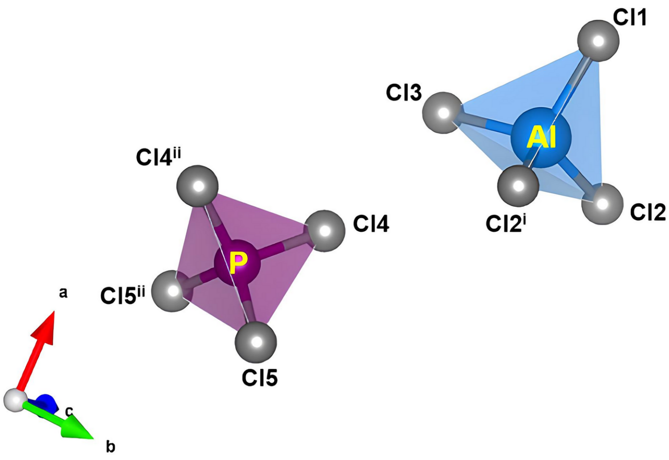

Figure 1
The local environments of the $AlCl_4$ (blue) and PCl_4 tetrahedra (purple) are shown. Symmetry codes correspond to those in Table 1.

Table 1
Selected 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) $x, y, -z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, -z+1$.

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 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, 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.

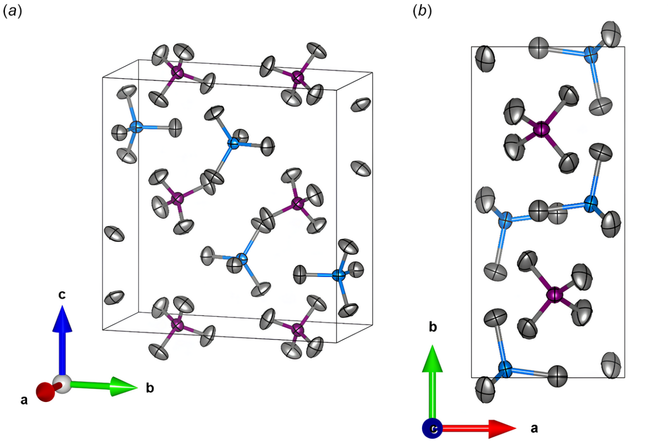

Figure 2
The displacement of ellipsoids of $AlPCl_8$ drawn at the 50% probability level viewed from two different orientations: (*a*) approximately along the [111] direction and (*b*) along the [001] direction. The $AlCl_4$ tetrahedra are represented in blue, and the PCl_4 tetrahedra in purple.

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	
Chemical formula	$PCl_4^{+}\cdot AlCl_4^{-}$
M_r	341.55
Crystal system, space group	Orthorhombic, *Pbcm*
Temperature (K)	293
a, *b*, *c* (Å)	6.2653 (6), 13.5033 (12), 14.0112 (13)
V (Å^3)	1185.38 (19)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	2.05
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.664, 0.671
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	38491, 1399, 1061
R_{int}	0.130
$(\sin \theta/\lambda)_{max}$ (Å^{-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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-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 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 $10° \leq 2\theta \leq 130°$, 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.

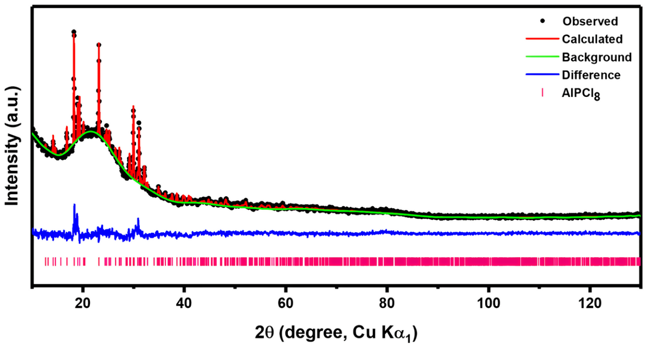

Figure 3
Powder X-ray Rietveld refinement profile of $AlPCl_8$. Black dots indicate the observed pattern, the red line represents the calculated pattern, the blue line shows the difference between the observed and calculated patterns, and the pink tick marks correspond to the Bragg reflections positions.

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Computing details

Phosphorus tetrachloride tetrachloridoaluminate

Crystal data

$PCl_4^+ \cdot AlCl_4^-$
$M_r = 341.55$
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) Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.914$ 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 × 0.2 × 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 $I > 2.0\sigma(I)$
$R_{int} = 0.130$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.0°$
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 18$

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 *w*ith the key S*I*GMA(/*F*O/) 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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å^2)

	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, º)

Al1—Cl2$^{\mathrm{i}}$	2.1223 (12)	P1—Cl5$^{\mathrm{ii}}$	1.9018 (12)
Al1—Cl1	2.1343 (16)	P1—Cl4$^{\mathrm{ii}}$	1.8959 (12)
Al1—Cl2	2.1223 (12)	P1—Cl4	1.8959 (12)
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Symmetry codes: (i) $x, y, -z+1/2$; (ii) $x, -y+3/2, -z+1$.