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ZnPCl$_7$: a compositionally and structurally unprecedented metal–phosphorus halide

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The synthesis and crystal structure of an unprecedented compound, zinc phosphorus heptachloride or *catena*-poly[phosphorus tetrachloride [[dichloridozinc]-μ-chlorido]], ZnPCl$_7$ or {[PCl$_4$][ZnCl$_3$]}$_n$, are reported. The reaction of ZnCl$_2$ with PCl$_5$ in a 1:1 molar ratio at 623 K produced single crystals of ZnPCl$_7$, which crystallizes in the orthorhombic space group *Ama2*. The Zn and P atoms lie on crystallographic mirror planes, as do four of the Cl atoms. One Cl atom lies on a twofold axis and one occupies a general position. Its extended structure features isolated [PCl$_4$]$^+$ tetrahedra and one-dimensional chains of corner-sharing ZnCl$_2$Cl$_{2/2}$ tetrahedra. Bond-valence sum calculations support the assignment of formal oxidation states. This discovery extends the compositional and structural landscape of mixed-metal halides.

1. Chemical context

Metal–phosphorus compounds have garnered interest owing to their diverse structures and potential functional properties (Chen *et al.*, 2023). In pursuit of discovering new compounds comprising a divalent metal and phosphorus within a halide framework, we investigated the solid-state reaction between zinc chloride (ZnCl$_2$) and phosphorus pentachloride (PCl$_5$). Heating a 1:1 stoichiometric mixture yielded a previously unreported compound, ZnPCl$_7$ (**I**), confirmed by a new powder X-ray diffraction pattern. Single-crystal growth enabled full structure determination, revealing both a new stoichiometry and a previously unobserved structure in the Zn–P–Cl chemical system.

2. Structural commentary

Compound (**I**) crystallizes in the orthorhombic space group *Ama2*, with one Zn (site symmetry *m*), one P (site symmetry *m*) and six Cl atoms (four with site symmetry *m*, one with site symmetry *2* and one on a general position) in the asymmetric unit (Fig. 1). The structure can therefore be formulated as ZnPCl$_7$ or $[\mathrm{ZnCl}_3]^-{}_n.n[\mathrm{PCl}_4]^+$.

The Zn^{2+} ion is tetrahedrally coordinated by four chloride anions (Table 1), with an average Zn—Cl bond distance of 2.2900 Å and Cl—Zn—Cl bond angles in the range 98.49 (4) to 118.60 (6)°. The P^{5+} atom forms a discrete [PCl$_4$]$^+$ tetrahedron with a shorter average P—Cl bond distance of 1.9286 Å and Cl—P—Cl angles clustered between 109.51 (9) and 110.20 (6)°. These bond lengths are consistent with expectations based on the sums of ionic radii (Shannon, 1976).

The extended structure of (**I**) consists of isolated PCl$_4$ units interspersed between infinite [100] chains of corner-sharing ZnCl$_2$Cl$_{2/2}$ tetrahedra (Fig. 2), forming a structure that is, to

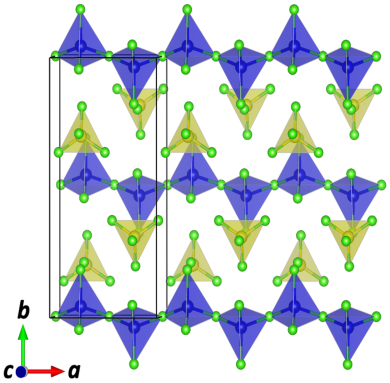

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Table 1
Selected geometric parameters (Å, °).

Zn1—Cl1	2.3689 (8)	P1—Cl4	1.937 (2)
Zn1—Cl2	2.2066 (14)	P1—Cl5	1.924 (2)
Zn1—Cl3	2.2223 (14)	P1—Cl6	1.9250 (13)
$Cl1^{i}$—Zn1—Cl1	98.49 (4)	$Cl6^{ii}$—P1—Cl6	107.69 (9)
Cl1—Zn1—Cl2	108.41 (3)	Cl4—P1—Cl6	110.20 (6)
Cl1—Zn1—Cl3	110.52 (3)	Cl5—P1—Cl6	109.61 (6)
Cl2—Zn1—Cl3	118.60 (6)	Zn1—Cl1—$Zn1^{iii}$	106.48 (5)
Cl4—P1—Cl5	109.51 (9)		

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$[PCl_4][ZnCl_3]$
M_r	344.51
Crystal system, space group	Orthorhombic, *Ama*2
Temperature (K)	293
a, *b*, *c* (Å)	7.1775 (5), 15.5212 (8), 9.0050 (4)
V ($Å^3$)	1003.19 (10)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	4.39
Crystal size (mm)	0.10 × 0.10 × 0.10
Data collection	
Diffractometer	Bruker D8 VENTURE
Absorption correction	Multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.64, 0.64
No. of measured, independent and observed [$I > 2.0\sigma(I)$] reflections	19802, 1627, 1467
R_{int}	0.050
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.712
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.060, 1.29
No. of reflections	1627
No. of parameters	52
No. of restraints	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.58, −0.55
Absolute structure	Parsons et al. (2013), 764 Friedel Pairs
Absolute structure parameter	0.016 (17)

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

our knowledge, unprecedented in metal–halide chemistry. Such a configuration – linking M^{2+} centered tetrahedra into chains and combining them with isolated X^{5+}-centered tetrahedra – has not been previously reported. To further validate the structural model, bond-valence-sum (BVS) calculations were performed using the *softBV* program (Chen *et al.*, 2019). The BVS values are in good agreement with the expected formal charges, further supporting the reliability of the refined structure: Zn +1.99, P +4.90, Cl1 −0.84, Cl2 −0.64, Cl3 −0.67, Cl4 −1.18, Cl5 −1.20 and Cl6 −1.17.

This type of one-dimensional chain of corner-sharing $ZnCl_4$ tetrahedra found in (**I**) is rarely observed in the halide system. Most known zinc chlorides, including $ZnCl_2$, form extended networks or layered structures rather than chains (Winkler *et al.*, 1959). Similar tetrahedral chain motifs have been reported in some oxides such as $Sr_2Fe_2O_5$ (D'Hondt *et al.*, 2008), but are extremely uncommon among halides.

3. Synthesis and crystallization

Anhydrous zinc chloride (Sigma-Aldrich, 98%) and phosphorus(V) chloride (Sigma-Aldrich, 95%) were used as received. A 1:1 molar mixture of $ZnCl_2$ (0.3952 g) and PCl_5 (0.6039 g) was thoroughly ground in an agate mortar and pressed into a pellet. The pellet was placed in a dried fused-silica ampoule, sealed under vacuum (∼360 Pa), and heated

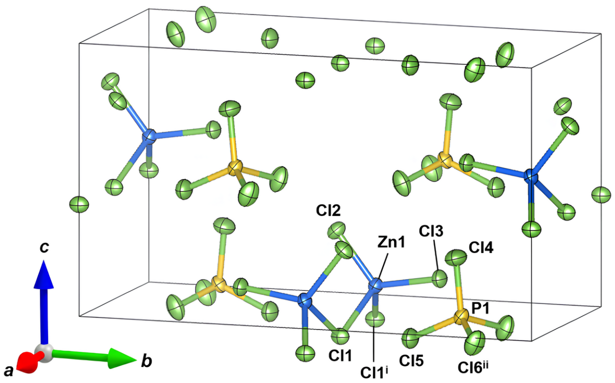

Figure 1
The crystal structure of (**I**) viewed approximately along the [100] direction. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x+\frac{1}{2}, y, z$; (ii) $-x+\frac{3}{2}, y, z$.

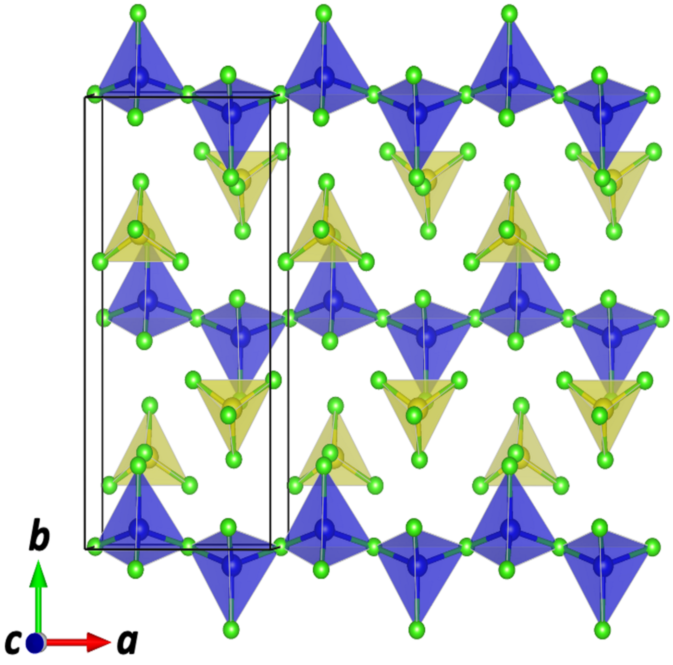

Figure 2
One-dimensional chains of corner-sharing $ZnCl_2Cl_{2/2}$ tetrahedra (blue) extending along the *a*-axis direction in the crystal structure of (**I**). The isolated PCl_4 tetrahedra are depicted in yellow.

from 303 K to 623 K at a rate of 5 K min^{-1}, and then slowly cooled to 373 K at a rate of 0.42 K min^{-1}, followed by natural cooling to room temperature.

Single crystals were isolated under an optical microscope in a dry room with a dew point of 223 K. $ZnPCl_7$ appears to be stable under dry-air conditions; therefore, all handling was carried out in a dry room. However, it is extremely sensitive to moisture and decomposed immediately upon exposure to humidity. A colourless crystal, approximately 0.1 mm in size, was placed into a 0.5 mm diameter glass capillary and sealed with capillary wax.

4. Refinement

Crystal data, data collection, and refinement parameters are summarized in Table 2.

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Computing details

(I)

Crystal data

[PCl$_4$][ZnCl$_3$]
M_r = 344.51
Orthorhombic, *Ama*2
Hall symbol: A 2 -2a
a = 7.1775 (5) Å
b = 15.5212 (8) Å
c = 9.0050 (4) Å
V = 1003.19 (10) Å^3
Z = 4
F(000) = 656
D_x = 2.281 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1767 reflections
θ = 3.9–31.3°
μ = 4.39 mm^{-1}
T = 293 K
Block, colourless
0.10 × 0.10 × 0.10 mm

Data collection

Bruker D8 VENTURE diffractometer
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.64, $T_{\max}$ = 0.64
19802 measured reflections
1627 independent reflections
1467 reflections with $I > 2.0\sigma(I)$
R_{int} = 0.050
$\theta_{\max}$ = 30.4°, $\theta_{\min}$ = 3.9°
$h = -10 \rightarrow 10$
$k = -21 \rightarrow 22$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.060
S = 1.29
1627 reflections
52 parameters
17 restraints
Primary atom site location: other
Method, part 1, Chebychev polynomial, (Watkin, 1994, *P*rince, 1982) [*w*eight] = 1.0/[A$_0$*T$_0$(x) + A$_1$*T$_1$(x) ··· + A$_{n-1}$]*T$_{n-1}$(x)] where A$_i$ are the Chebychev coefficients listed below *w* and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A$_i$ are: 20.3 28.2 14.3 4.23 0.510
$(\Delta/\sigma)_{\max}$ = 0.0003
$\Delta\rho_{\max}$ = 0.58 e Å^{-3}
$\Delta\rho_{\min}$ = −0.55 e Å^{-3}
Absolute structure: Parsons et al. (2013), 764 Friedel Pairs
Absolute structure parameter: 0.016 (17)

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

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Zn1	0.2500	0.53981 (3)	0.06695 (9)	0.0283
P1	0.7500	0.80615 (8)	0.04103 (15)	0.0301
Cl1	0.5000	0.5000	−0.09048 (14)	0.0318
Cl2	0.2500	0.45321 (9)	0.26129 (16)	0.0370
Cl3	0.2500	0.68125 (8)	0.10522 (15)	0.0394
Cl4	0.7500	0.79444 (11)	0.25514 (17)	0.0538
Cl5	0.7500	0.69371 (10)	−0.04891 (18)	0.0503
Cl6	0.53345 (16)	0.86924 (7)	−0.02285 (15)	0.0535

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0314 (3)	0.0250 (2)	0.0284 (3)	0.0000	0.0000	0.0023 (2)
P1	0.0314 (6)	0.0273 (6)	0.0316 (7)	0.0000	0.0000	0.0072 (5)
Cl1	0.0238 (5)	0.0414 (6)	0.0302 (5)	0.0025 (5)	0.0000	0.0000
Cl2	0.0380 (7)	0.0381 (7)	0.0351 (6)	0.0000	0.0000	0.0125 (6)
Cl3	0.0563 (9)	0.0257 (5)	0.0363 (7)	0.0000	0.0000	−0.0015 (5)
Cl4	0.0756 (12)	0.0546 (9)	0.0314 (7)	0.0000	0.0000	0.0058 (7)
Cl5	0.0740 (11)	0.0308 (7)	0.0461 (9)	0.0000	0.0000	0.0001 (6)
Cl6	0.0385 (5)	0.0465 (6)	0.0753 (8)	0.0087 (5)	−0.0050 (5)	0.0161 (5)

Geometric parameters (Å, º)

Zn1—Cl1$^{\rm i}$	2.3689 (8)	P1—Cl6$^{\rm ii}$	1.9250 (13)
Zn1—Cl1	2.3689 (8)	P1—Cl4	1.937 (2)
Zn1—Cl2	2.2066 (14)	P1—Cl5	1.924 (2)
Zn1—Cl3	2.2223 (14)	P1—Cl6	1.9250 (13)
Cl1$^{\rm i}$—Zn1—Cl1	98.49 (4)	Cl6$^{\rm ii}$—P1—Cl5	109.61 (6)
Cl1$^{\rm i}$—Zn1—Cl2	108.41 (3)	Cl4—P1—Cl5	109.51 (9)
Cl1—Zn1—Cl2	108.41 (3)	Cl6$^{\rm ii}$—P1—Cl6	107.69 (9)
Cl1$^{\rm i}$—Zn1—Cl3	110.52 (3)	Cl4—P1—Cl6	110.20 (6)
Cl1—Zn1—Cl3	110.52 (3)	Cl5—P1—Cl6	109.61 (6)
Cl2—Zn1—Cl3	118.60 (6)	Zn1—Cl1—Zn1$^{\rm iii}$	106.48 (5)
Cl6$^{\rm ii}$—P1—Cl4	110.20 (7)		

Symmetry codes: (i) −*x*+1/2, *y*, *z*; (ii) −*x*+3/2, *y*, *z*; (iii) *x*+1/2, −*y*+1, *z*.