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p-Phenylenediammonium tetrachlorozincate(II)

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The structure of the title compound, $(C_6H_{10}N_2)[ZnCl_4]$, contains simple $ZnCl_4$ tetrahedra in the *bc* plane creating alternating layers of organic and inorganic sublattices, a feature that is very common for compounds of this type. The two sublattices are held together by coulombic attraction of the cationic organic sublattice and anionic inorganic sublattice and also by hydrogen bonding. The anions are located on general positions. The cations, however, are located on mirror planes. As a result, there are two half-cations in the asymmetric unit.

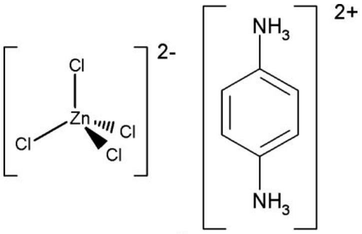
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.079
Data-to-parameter ratio = 23.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

We have explored synthetic methodologies (Bringley & Liebert, 2003, Bringley *et al.*, 2005) whereby amine-containing molecules may be assembled *via* coulombic attraction to inorganic anions of opposite charge, at low pH. In this manner ‘pieces or slices’ of an inorganic sublattice having a net charge are stabilized by a counter-charged organic sublattice, typically organoammonium or phosphonium cations. These organic–inorganic hybrids may then be ‘disassembled’ as a function of pH because deprotonation of the amine molecules destroys the coloumbic attraction between the sublattices and leads to dissociation of the complex. Such materials are potentially useful as switchable release vehicles in photography and in drug delivery (Bringley & Liebert, 2003, Bringley *et al.*, 2005). We report here the synthesis and structure of 1,4-phenylenediammonium tetrachlorozincate(II), a self-assembled structure of zinc chloride and the photographic color developer paraphenylenediamine. The structure contains simple $ZnCl_4$ tetrahedra that order in the *bc* plane, creating alternating layers of organic and inorganic sublattices, a feature that is very common for compounds of this type, *e.g.* diethylenediammonium tetrachlorozincate(II) chloride (Walha *et al.*, 1998), bis(*n*-heptylammonium) tetrachlorozincate(II) (Guo *et al.*, 1995), and other related ammonium tetrachlorozincates (Caëtano *et al.*, 1995; Blachnik *et al.*, 2000). The crystal packing is stabilized by N—H···Cl hydrogen bonds (Table 1).



(I)

Experimental

Crystals of the title complex suitable for single-crystal X-ray diffraction were prepared as follows: ZnO (2.00 g, 24.6 mmol) was dissolved in hot 85% H_3PO_4 (10.0 ml). Paraphenylenediamine dihydrochloride (4.45 g, 24.6 mmol) was dissolved in distilled water (20 ml) and 85% H_3PO_4 (3 ml). The two solutions were then combined slowly and allowed to cool. After one month, large light-green crystals were collected by vacuum filtration.

Crystal data

$(C_6H_{10}N_2)[ZnCl_4]$
$M_r = 317.33$
Orthorhombic, $Cmc2_1$
$a = 19.733\ (4)$ Å
$b = 13.083\ (3)$ Å
$c = 9.6430\ (19)$ Å
$V = 2489.5\ (9)$ Å^3
$Z = 8$
$D_x = 1.693$ Mg m^{-3}
Mo *Kα* radiation
$\mu = 2.79$ mm^{-1}
$T = 293\ (2)$ K
Plate, green
0.15 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.381$, $T_{\max} = 0.564$ (expected range = 0.588–0.870)
34863 measured reflections
2867 independent reflections
2689 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.079$
$S = 1.06$
2867 reflections
121 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 2.3296P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}
Absolute structure: Flack (1983), 1305 Friedel pairs
Flack parameter: 0.398 (16)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl2$^{\rm i}$	0.89	2.31	3.180 (3)	165
N1—H1*B*···Cl2$^{\rm ii}$	0.89	2.39	3.279 (3)	178
N1—H1*C*···Cl4$^{\rm iii}$	0.89	2.62	3.326 (3)	137
N1—H1*C*···Cl3	0.89	2.82	3.258 (3)	112
N2—H2*A*···Cl1	0.89	2.32	3.199 (3)	172
N2—H2*B*···Cl1$^{\rm iv}$	0.89	2.59	3.222 (3)	129
N2—H2*B*···Cl4$^{\rm v}$	0.89	2.82	3.460 (4)	130
N2—H2*C*···Cl4$^{\rm iii}$	0.89	2.39	3.270 (4)	168

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

H atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.89 Å) and allowed to ride on their parent atoms, with $U_{\rm eq}$(H) =1.2$U_{\rm eq}$(C) and 1.5$U_{\rm eq}$(N). The ammonium groups were allowed to rotate but not to tip. The structure is an inversion twin with a ratio of twin components of 0.398 (16)/0.602 (16). The maximum residual density peak is 2.86 Å from atom H6 atom.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Materials Studio* (Accelrys, 2002); software used to prepare material for publication: *SHELXTL*; molecular graphics: *SHELXTL* and *Materials Studio*.

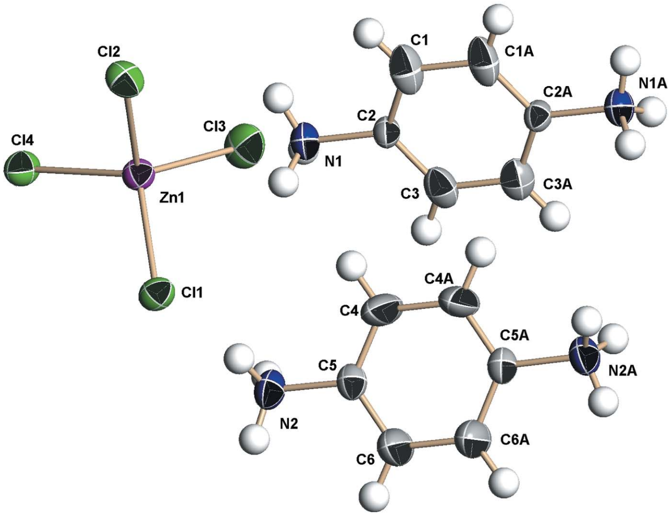


Figure 1
A view of compound (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $1 - x, y, z$.]

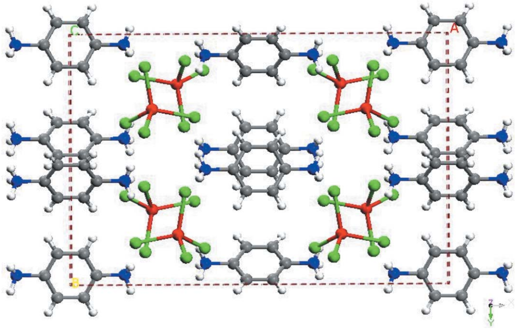


Figure 2
The unit cell contents, illustrating alternating layers of organic and inorganic sublattices. Zn = red, Cl = green, C = gray, N = blue.

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