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p-Phenylenediammonium tetraiodozincate(II) dihydrate

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The title compound, $(C_6H_{10}N_2)[ZnI_4]\cdot 2H_2O$, crystallizes as an organic–inorganic hybrid. The ionic layer consists of isolated ZnI_4 tetrahedra. The hydrocarbon layer has two symmetry-independant centrosymmetric *p*-phenylenediammonium cations that link to the ionic layer *via* hydrogen bonding. Two water molecules of hydration lie between the anion and the two cations.

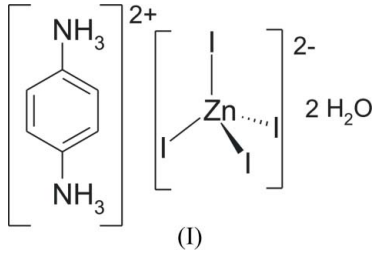
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.027
wR factor = 0.071
Data-to-parameter ratio = 24.1

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

Comment

In recent years, a significant number of organic–inorganic hybrid materials based on metal halide units have been prepared and studied; for reviews, see Papavassiliou (1997) and Mitzi (1999). It has been shown that their structures can vary considerably, ranging from systems based on isolated molecules to ones containing extended chains as in $(Me_4N)[PbI_3]$(Contreras *et al.*, 1983) and up to two- or three-dimensional networks (Mitzi, 1999). Very few cases have been reported of the zero-dimensional form, in which the metal halide units exist isolated from each other and connect *via* hydrogen bonds to the organic counter-ion. Often, water molecules are able to coordinate to the two charged components, as in $(CH_3NH_3)_4[PbI_6]\cdot 2H_2O$ (Vincent *et al.*, 1986). $[ZnI_4]^{2-}$ usually consists of iodides tetrahedrally bonded to the zinc. The counter-ions contain tertiary or quaternary ammonium ions, which then hydrogen bond to the iodides, *e.g.* $(C_{11}H_{13}N_2)^+$ (Orioli & Lip, 1974), $[N(CH_3)_4]^+$ (Werk *et al.*, 1990) and $[N(C_2H_5)_4]^+$ (Harrison *et al.*, 2000). The structure of *p*-phenylenediammonium tetraiodozincate(II) dihydrate, (I), is the first reported case with primary ammonium cations as the counter-ion.



(I)

The unit cell of (I) contains two ZnI_4 tetrahedra, with one lying at $z \simeq \frac{1}{4}$ pointing along the negative c axis and the other at $z \simeq \frac{3}{4}$ towards the positive c axis (Fig. 2). The bond distances and angles are in similiar ranges to those of previously reported tetrahedra. Two short [2.6043 (16) and 2.6081 (12) Å] and two long [2.6236 (15) and 2.6274 (13) Å] distances cause a slight deviation of the ideal geometry. There are two unique *p*-phenylenediammmonium cations in the

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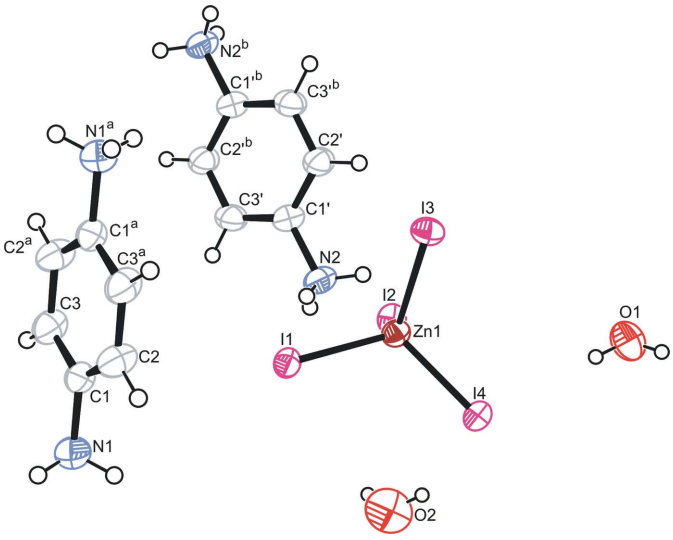

Figure 1
The asymmetric unit of (I) and some adjacent atoms, showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Atoms labelled with the superscripts 'a' and 'b' are at the symmetry positions $(1-x, -y, 2-z)$ and $(-x, -y, 1-z)$, respectively.

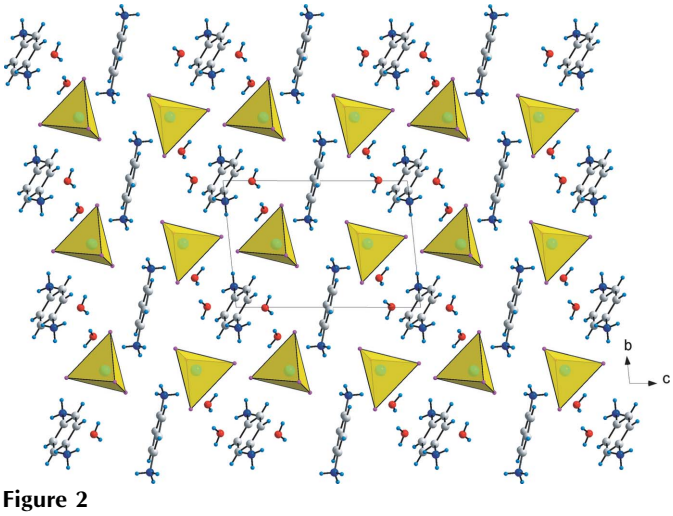

Figure 2
The arrangement of ions of (I), projected along the *a* axis.

asymmetric unit (Fig. 1). Cation 1 sits on the inversion centre at $(\frac{1}{2}, 0, 1)$ and cation 2 on another at $(0, 0, \frac{1}{2})$. There are also two water molecules of hydration. Atom O1 sits close to the *ac* plane and O2 is located completely in the unit cell.

Cation 1 has one simple hydrogen bond to I2 and two to O1. Cation 2 has a more complex pattern, with two long bifurcated bonds to I3 and I3^{iii}, a short simple one to I1 and a second bifurcated bond to two different acceptor toms O2^{i} and I4^{i} (Fig. 3) (symmetry codes as in Table 2). The N—H···O$_w$ distances are in the range 2.05–2.19 Å, slightly longer than the maximum given by Steiner (2002) in his review of the hydrogen bond in the solid state. The O2 water molecule hydrogen bonds to the I atoms as well. The hydrogen-bond acceptor distances O2$_w$—H···I are longer than the average of 2.68 (1) Å quoted by Steiner (2002), but the O2$_w$···I distances comply with the average of 3.61 (1) Å (see Table 2). The

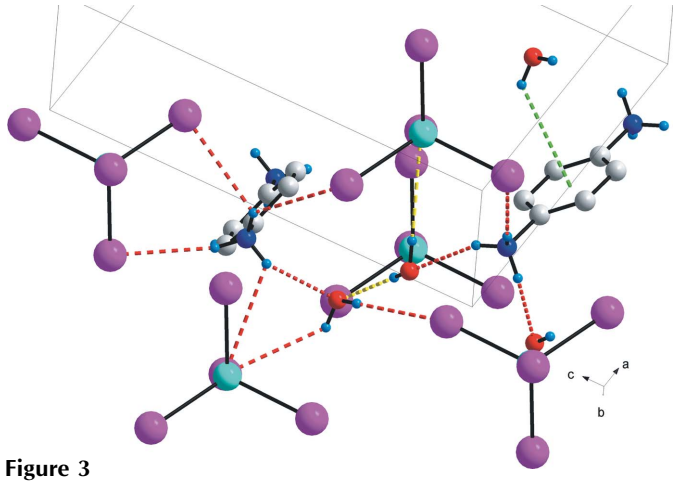

Figure 3
Hydrogen-bonding (dashed lines) pattern between the I, O and N atoms (red lines), weak interactions between water and iodide (yellow lines) and the O—H···π shown with a green line.

second water of hydration has O1$_w$···I distances of 3.923 (5) and 4.034 (6) Å, and can be considered weak interactions. An O—H···π interaction occurs between O2 and cation 1 with a distance of 3.22 Å from H22 to the ring centroid.

Experimental

Crystals of (I) were grown at room temperature by first dissolving ZnI_2 (0.225 g, 0.708 mmol) in ethanol (14 ml) and 57% HI (0.600 g). Then, $NH_3C_6H_4NH_3$ (0.080 g, 0.726 mmol) was added. The crystals, grown by slow evaporation, were harvested after 14 d. A colourless crystal suitable for X-ray diffraction studies was selected and studied. Analysis calculated for $C_6H_{14}I_4N_2O_2Zn$: C 10.02, H 1.96, N 3.90%; found: C 10.95, H 2.01, N 4.45%.

Crystal data

$(C_6H_{10}N_2)[ZnI_4]\cdot 2H_2O$	$Z = 2$
$M_r = 719.16$	$D_x = 2.787$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 8.398$ (5) Å	Cell parameters from 927 reflections
$b = 8.611$ (5) Å	$\theta = 2.6$–$28.2°$
$c = 12.540$ (5) Å	$\mu = 8.63$ mm^{-1}
$\alpha = 92.821$ (5)°	$T = 293$ (2) K
$\beta = 103.344$ (5)°	Plate, colourless
$\gamma = 102.407$ (5)°	0.35 × 0.20 × 0.08 mm
$V = 857.1$ (8) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	3352 independent reflections
φ and ω scans	2967 reflections with $I > 2\sigma(I)$
Absorption correction: integration (*XPREP*; Bruker, 1999)	$R_{int} = 0.034$
$T_{min} = 0.152$, $T_{max} = 0.545$	$\theta_{max} = 26°$
5108 measured reflections	$h = -9 \rightarrow 10$
	$k = -10 \rightarrow 7$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 1.4644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.071$	$\Delta\rho_{max} = 1.01$ e Å^{-3}
$S = 1.08$	$\Delta\rho_{min} = -0.65$ e Å^{-3}
3352 reflections	Extinction correction: *SHELXL97*
139 parameters	Extinction coefficient: 0.0036 (3)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

C1′—N2	1.468 (6)	Zn1—I1	2.6081 (12)
C1—N1	1.466 (7)	Zn1—I3	2.6236 (15)
Zn1—I4	2.6043 (16)	Zn1—I2	2.6274 (13)
I4—Zn1—I1	114.06 (4)	I4—Zn1—I2	106.87 (3)
I4—Zn1—I3	109.25 (3)	I1—Zn1—I2	107.10 (3)
I1—Zn1—I3	108.64 (4)	I3—Zn1—I2	110.91 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···I2^{i}	0.89	2.76	3.620 (5)	162
N1—H1*B*···O1^{i}	0.89	2.16	2.995 (7)	157
N1—H1*C*···O1^{ii}	0.89	2.05	2.871 (7)	153
N2—H2*A*···I3^{iii}	0.89	3.14	3.809 (5)	133
N2—H2*A*···I3	0.89	3.19	3.701 (5)	119
N2—H2*B*···I1	0.89	2.81	3.681 (5)	166
N2—H2*C*···O2^{i}	0.89	2.19	2.966 (7)	145
N2—H2*C*···I4^{i}	0.89	3.21	3.703 (5)	117
O1—H12···I4	0.85	3.07	3.923 (5)	180
O1—H11···I3^{iv}	0.85	3.18	4.034 (6)	180
O2—H21···I2^{v}	0.85	2.77	3.554 (5)	156
O2—H22···I4	0.85	2.98	3.606 (6)	132

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y-1, z+1$; (iii) $-x, -y+1, -z+1$; (iv) $x, y+1, z$; (v) $-x+1, -y+1, -z$.

All H atoms were found in a difference map. For the H atoms bonded to O atoms, restraints were used to obtain reasonable details of O—H distances and H—O—H angles. Finally these H atoms were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(O)$. The remaining H atoms were refined in idealized positions in the riding-model approximation and with $U_{iso}(H) = 1.2U_{eq}$(aromatic C, N). The NH_3 groups were allowed to rotate but not to tip. The highest residual peak is located 0.78 Å from atom I2.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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